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Soft X-Ray and Vacuum Ultraviolet Based Spectroscopy of the Actinides

J. G. Tobin

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8th School on the Physics and Chemistry of the Actinides
Stara Lesna, Slovakia
April 7, 2011 through April 9, 2011

Disclaimer

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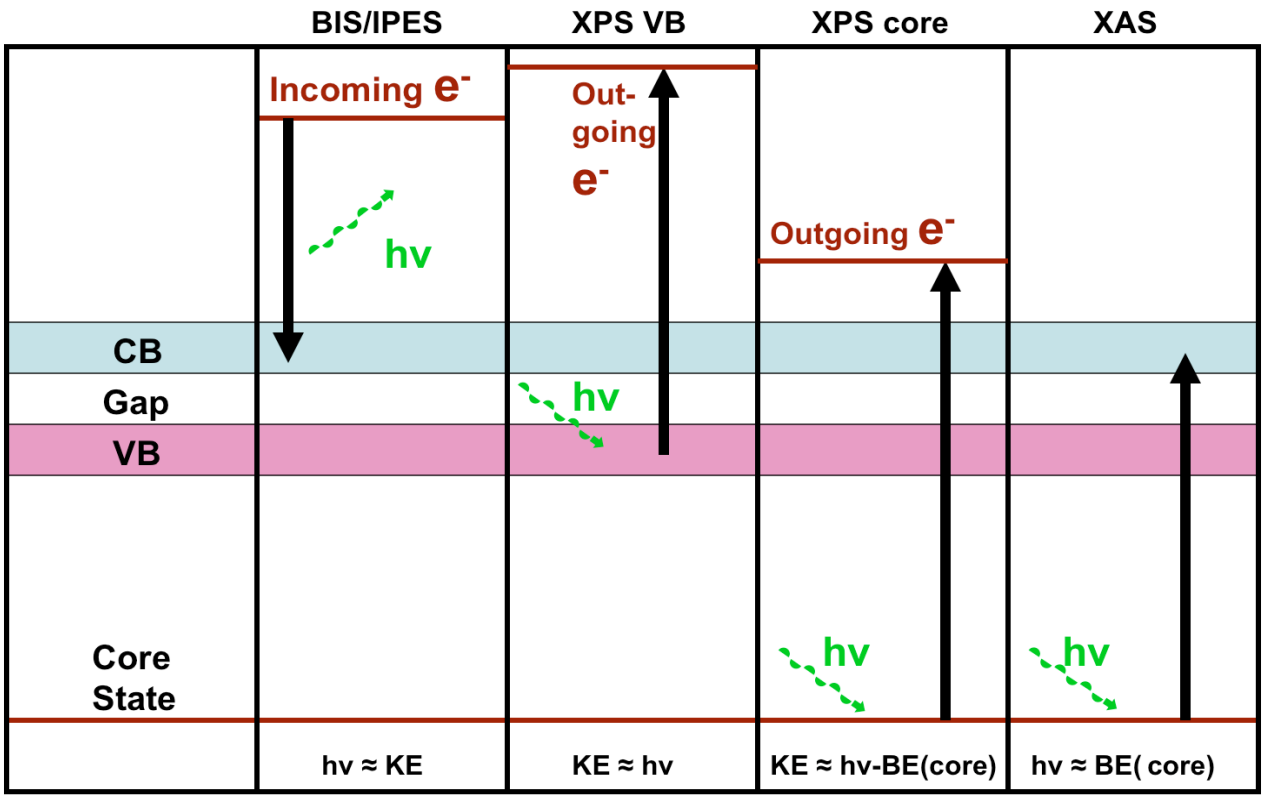
Motivation and Overview

- Most demanding & powerful actinide spectroscopy → soft x-ray and VUV photons
- Relatively low energy and fairly small sampling depth:
  → un-encapsulated, highly cleaned and well prepared surface
  → myriad of sample containment problems for radioactive materials
- **Despite these hindrances and difficulties, the soft-x-ray and ultra-violet spectroscopy of the actinides can provide an amazing level of detailed information, particularly having to do with 5f electronic structure.**
- The subjects of discussion will include:
  - VUV photoelectron spectroscopy (PES)
  - X-ray photoelectron spectroscopy (XPS)
  - Synchrotron-radiation-based photoelectron spectroscopy
  - Soft x-ray absorption spectroscopy (XAS)
  - Soft x-ray emission spectroscopy (XES)
  - Inverse photoelectron spectroscopy (IPES)
    Bremstrahlung Isochromat Spectroscopy (BIS)
    Low energy IPES
    Resonant inverse photoelectron spectroscopy (RIPES).

Comparison of Processes: BIS, XPS and XAS

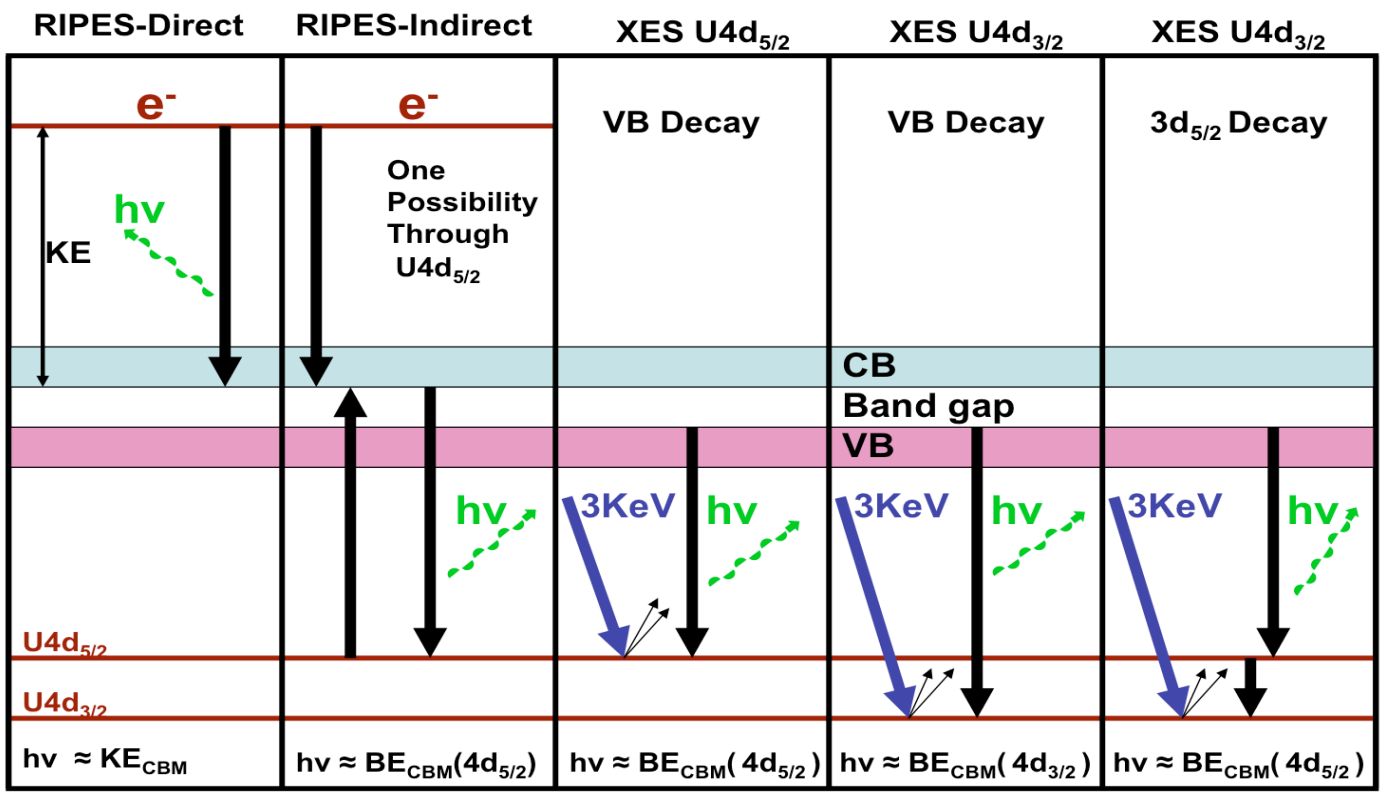


- XPS, UPS and PES sample the occupied DOS or Valence Band (VB)
- BIS and XAS sample the unoccupied DOS or Conduction Band (CB)

Photon absorption and emission:

electric dipole transitions with Δl = +/- 1

Comparison of Processes: RIPES and XES in UO_2

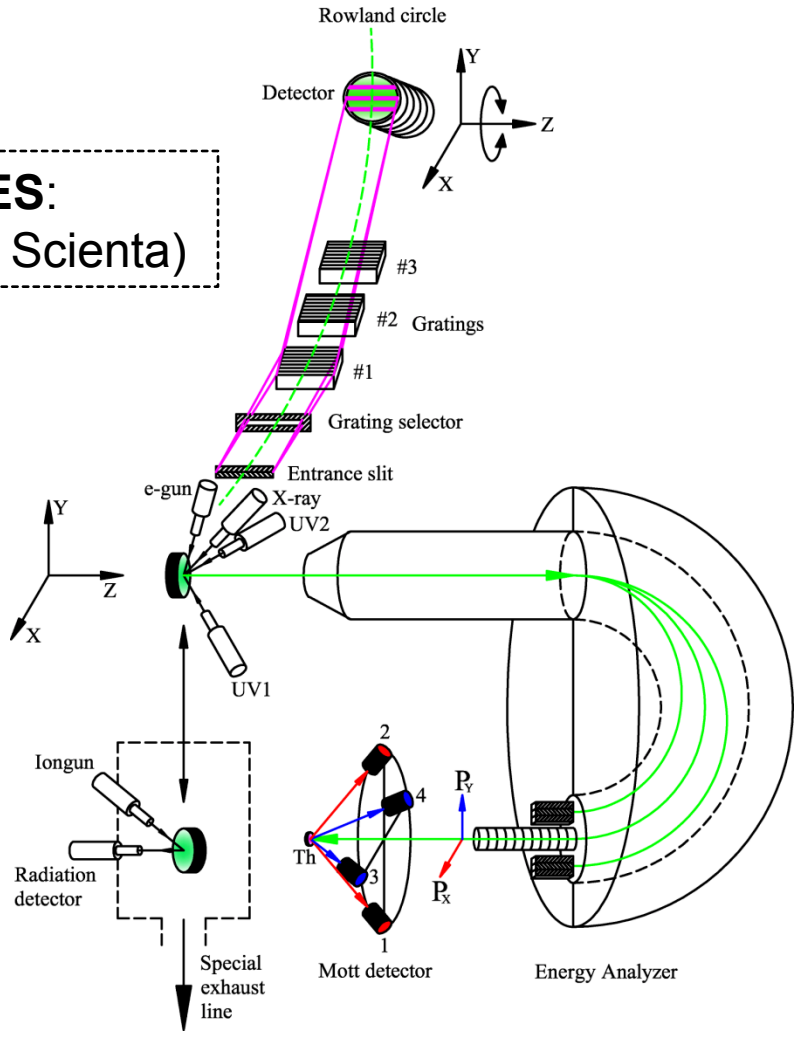


- **XES samples the occupied DOS or Valence Band (VB)**
- **RIPES samples the unoccupied DOS or Conduction Band (CB)**

Photon emission: electric dipole transitions with Δl = +/- 1

Experimental setup at LLNL for actinides research

BIS and RIPES:
XES 350 (VG Scienta)



Sample handling system for actinides

Photoelectron Spectroscopy, with spin and without spin (multichannel)

SRPES:
Phoibos 150 with Mott detection (Specs)

Fano Spectroscopy with the chirally configured He UPS sources

XPS with the X-ray tube, AlKα and MgKα

Hidden role of electrons: limiting sampling depth

- **While soft x-rays and vacuum ultra-violet radiation have limited penetration and escape depths, it is the mean free paths of the electrons that actually are the greatest limitation.**
- **Trelenberg et al, Surface Science 600, 2338 (2006)**
- **Bedrossian et al, MRS Symp. Proc. 437, 79 (1996): TEY MFP = 22Å**

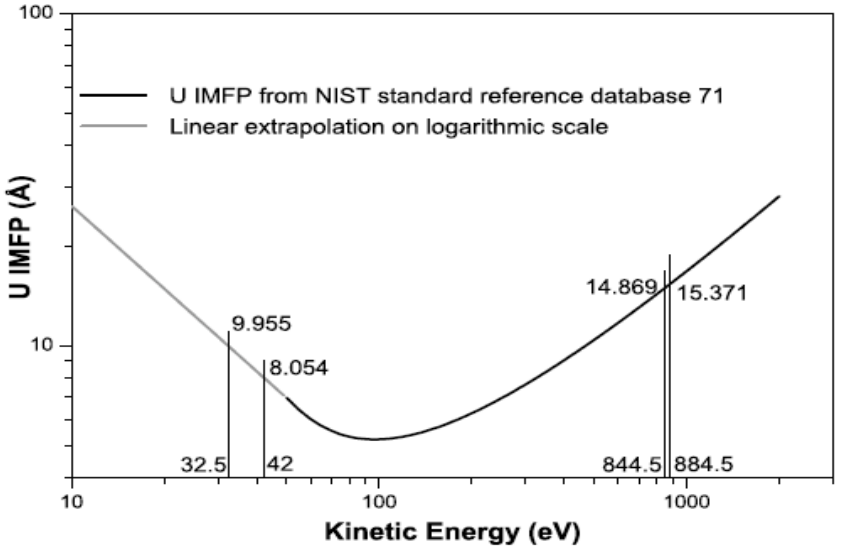
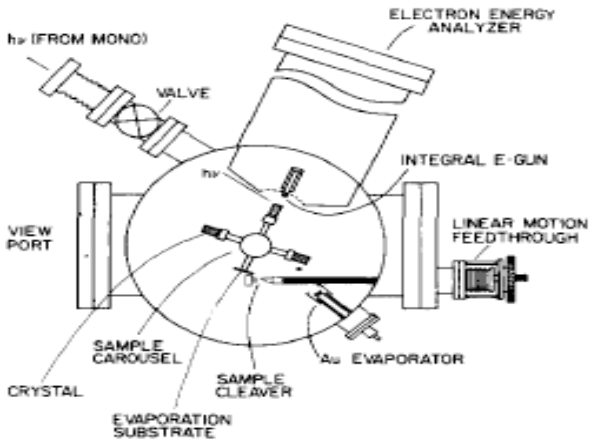


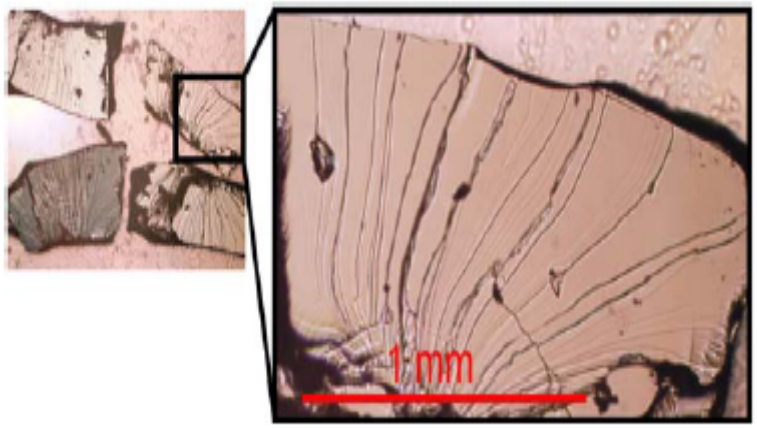
Fig. 7. Electron inelastic mean free path (IMFP) vs. kinetic energy for uranium. IMFP value values from 2000 eV to 50 eV taken from NIST database #71 [26]; values less than 50 eV were extrapolated from the database values.

If the measured x-ray absorption signal arising from a depth z in the specimen for a given white line energy is proportional to $I(z)\ Exp(-z/\mu)$, then the measured, relative intensities of the absorption edges of Ni, Fe, and Co in the spectra are consistent with $\mu \approx 22$Å. The Cu spacer layer, which is buried under at least 13Å of Co and 50Å of Permalloy in each specimen, does not contribute appreciably to the absorption signal. Therefore, the MXCD measurement detects *not* the average magnetic response of different layers but rather the magnetic moment present in the outermost layer for each magnetic element.

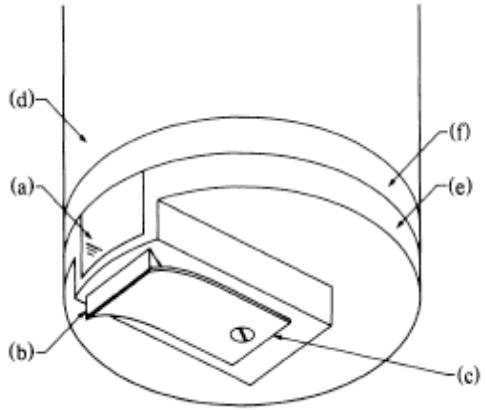
Sample prep: cleaving crystals, following the HTSC example



Spicer et al, Thin Solid Films 56, 1 (1979)



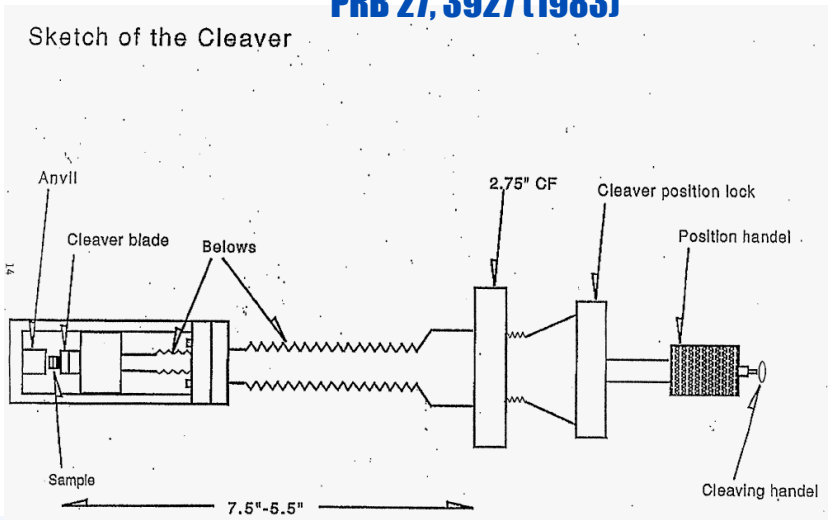
Barisic et al, SLAC-PUB-13412, Sept 2008



Hanemane & Bachrach, PRB 27, 3927 (1983)

- This is a very good way to make clean samples.
- The trick is to get a good cleavage plane.
- UWSRC experiments were often cleaved samples. (Olson & LANL).

"Safety Procedures for the Electron Spectroscopy of Actinides at the ALS," D.K. Shuh, N.M. Edelstein, and J.J. Bucher Chemical Sciences Division LBNL-39909, UC-401 (1966); J. Allen & J. Denlinger



Sample prep: thin film deposition, e.g. via plasmas

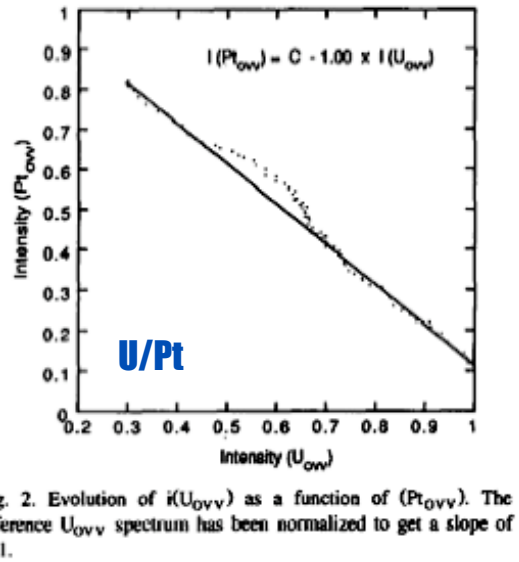
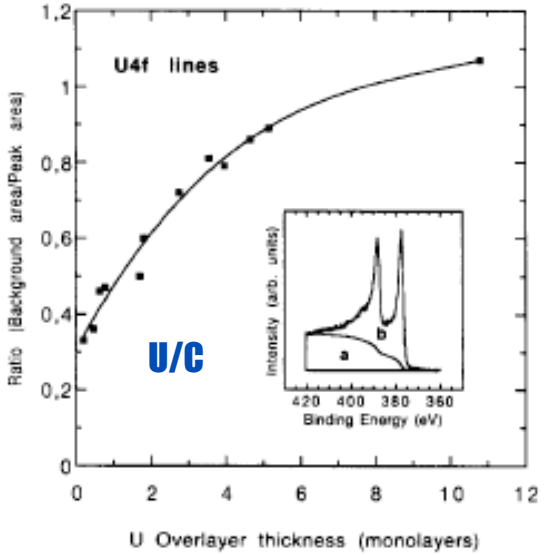


Fig. 2. Evolution of $i(U_{ovv})$ as a function of (Pt_{ovv}). The reference U_{ovv} spectrum has been normalized to get a slope of −1.

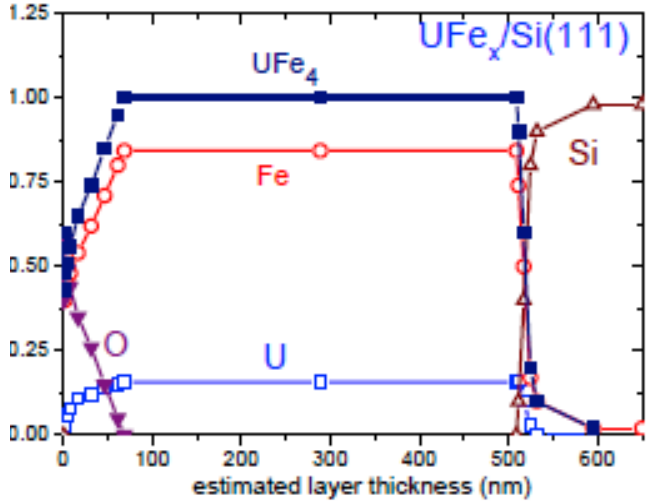
Gouder & Comenares,

Surf. Sci.341, 51 (1995)



Gouder, Comenares & Naegele,

Surf. Sci. 342, 299 (1995)



Adamska, Havela, Gouder et al

J. Phys. Conf Series 200, 012057 (2010)

- As with Rare Earths, vapor deposition is an excellent way to make clean actinide samples
- ITU has a long track record of vapor deposition using plasmas, including Pu and Am.

Sample Prep: laser ablation at LLNL

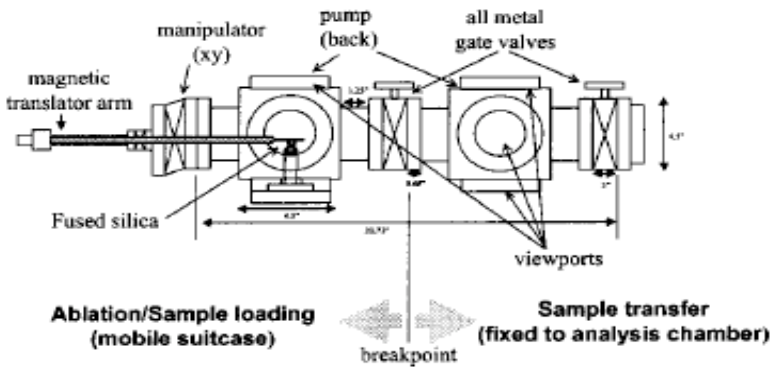


FIG. 3. Laser ablation/sample transfer schematic showing the mobile suitcase as well as the sample transfer chamber, which is attached to the main analysis chamber (not shown).

Trelenberg et al, Rev. Sci. Instrum. 75, 713 (2004)

Trelenberg et al, Surface Science 600, 2338 (2006)

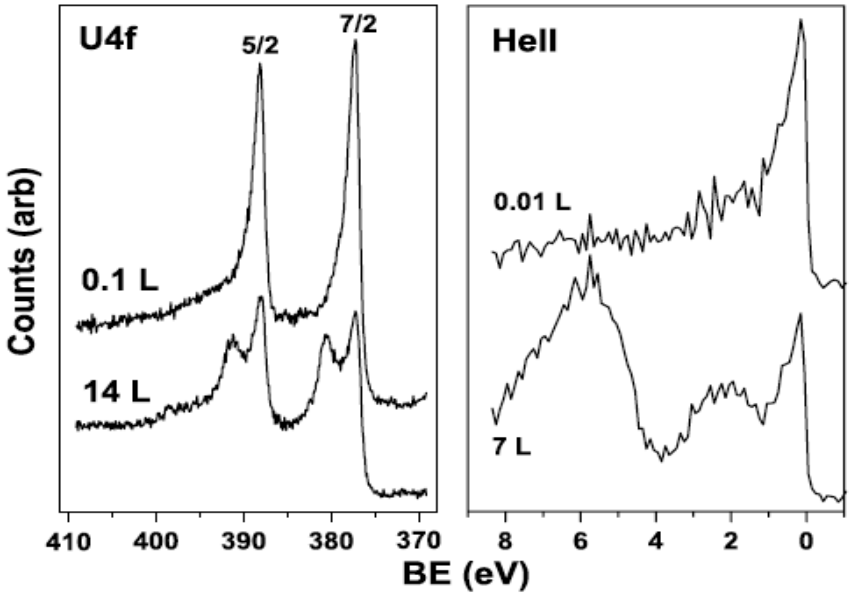
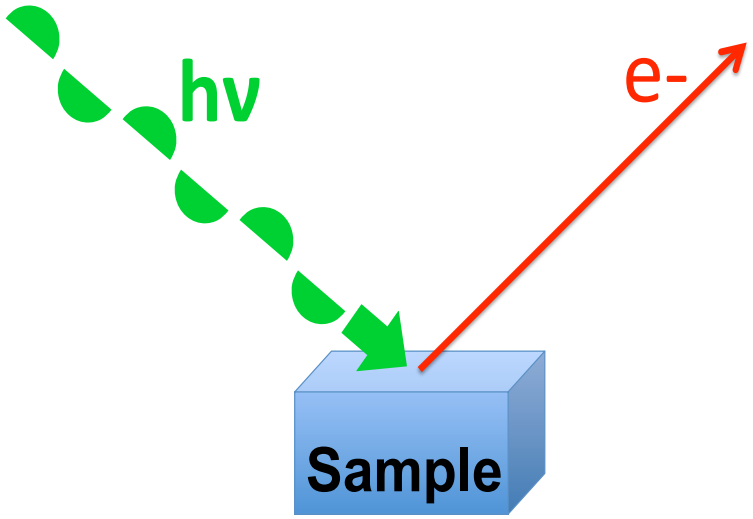


Fig. 1. Photoemission from both the U4f core level (Mg Kα XPS) and the Fermi level (He II UPS) show an unoxidized uranium surface produced by laser ablation (upper scans). With exposure over time additional peaks are seen (U4f: ~380 and 391 eV; Fermi: ~2 and 6 eV).

- As a test for possibly depositing Pu, U nanoscale films were prepared in situ using laser ablation.
- The oxidation of the U films was also studied.

Photoelectron Spectroscopy (PES), including X-ray PES or XPS and Ultraviolet PES or UPS



Select energy (and direction) of electrons

Laboratory Sources

XPS AlKα hν = 1487 eV

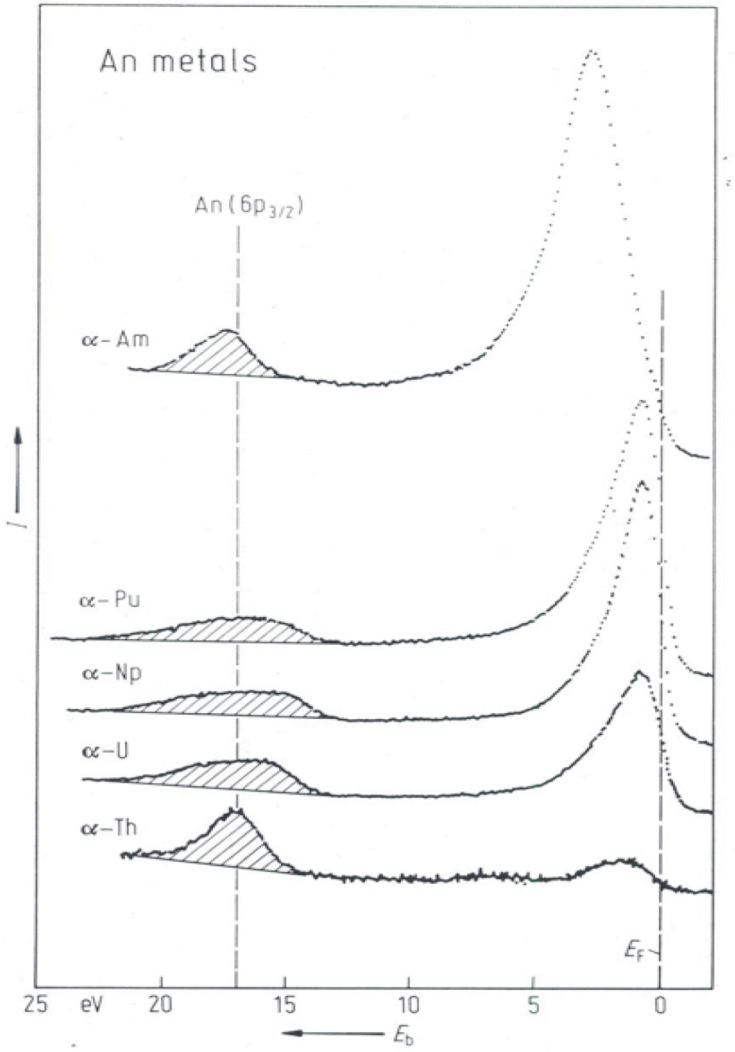
XPS MgKα hν = 1253 eV

UPS HeII = 40.8 eV

UPS HeI = 21.22 eV

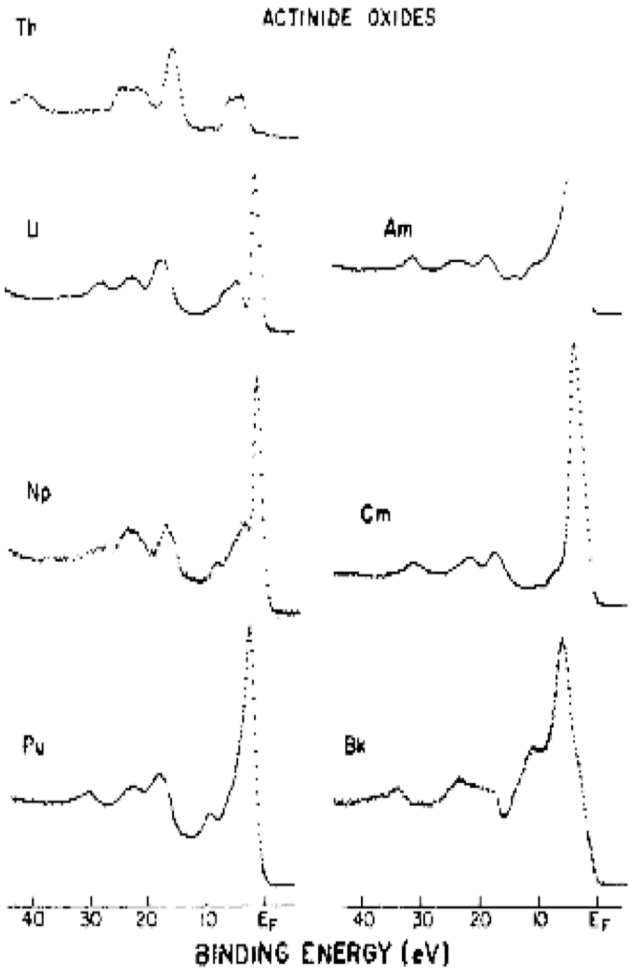
$$h\nu = KE_e + B^F + \Phi$$

Pioneering Work- XPS in Naegele's Review



- XPS spectra of Naegele
- This beautiful data was unpublished until 1994: it may be quite a bit older.
- The reference below is a treasure chest of spectra, many unpublished otherwise or in difficult-to-find conference proceedings.
- J. R. Naegele, *Actinides and some of their alloys and compounds*, Electronic Structure of Solids: Photoemission Spectra and Related Data, Landolt-Bornstein *Numerical Data and Functional Relationships in Science and Technology*, ed. A Goldmann, Group III, Volume **23b**, Pages 183 - 327 (1994).

Pioneering Work-XPS of Actinide Oxides by Veal and Lam in the 1970s



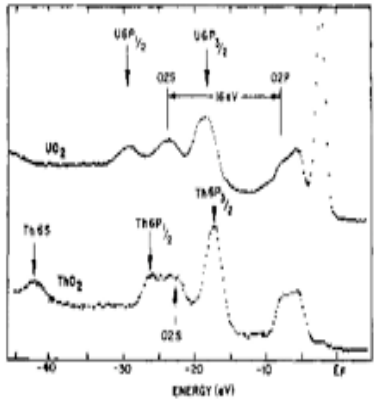


FIG. 4. XPS spectra of UO_2 and ThO_2 within 45 eV of the Fermi energy. The narrow peak in UO_2 near E_F is associated with the 5*f* electrons.

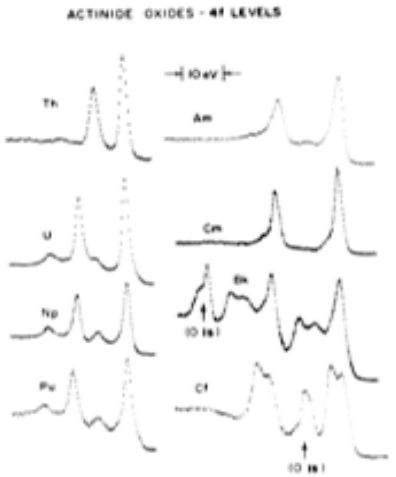
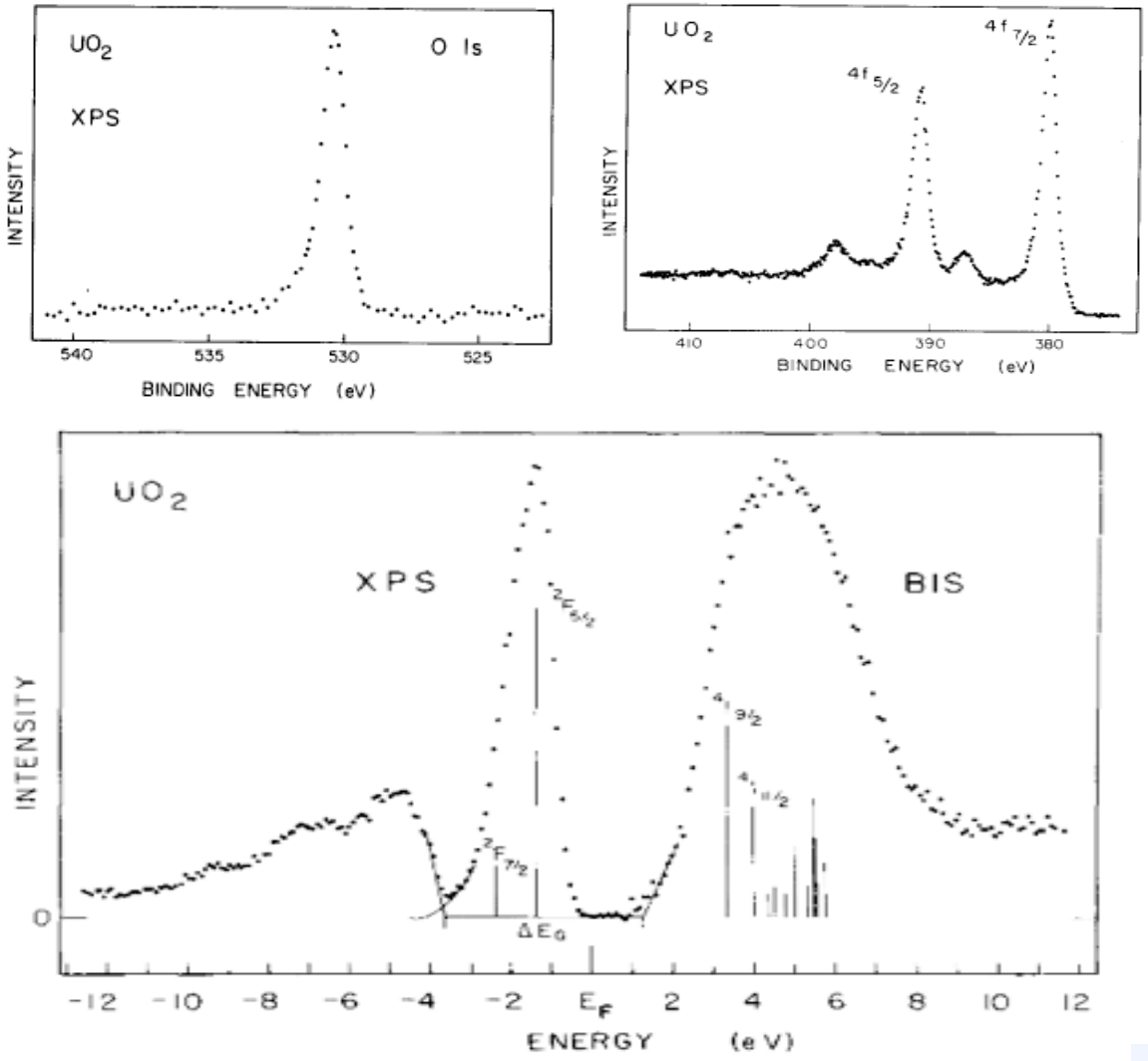


FIG. 3. Actinide 4*f* core-level spectra recorded for oxides of the elements thorium through californium.

These assignments and spectra are still correct.

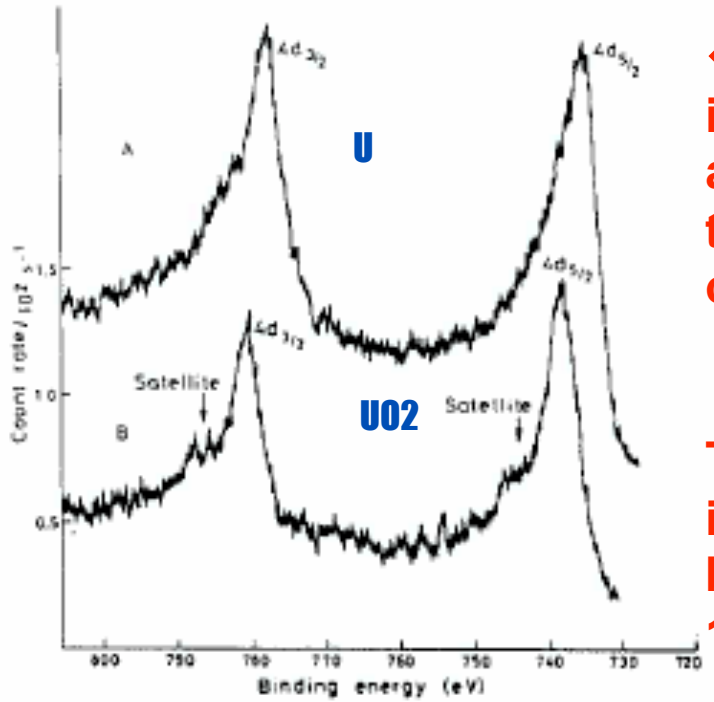
B. W. Veal, D. J. Lam, H. Diamond, and H. R. Hoekstra, Phys. Rev. B 15, 2929 (1977); B. W. Veal and D. J. Lam, Phys. Rev. B 10, 4902 (1974); B. W. Veal and D. J. Lam, Phys. Lett. 49A, 466 (1974).

Pioneering Work-BIS and XPS of UO_2 by Baer and Schoenes



- The XPS was high resolution, using monochromatized AlKα (1487eV)
- The BIS is done by running the XPS machine backwards, therefore it is at the AlKα energy
- Y. Baer and J. Schoenes, Solid State Commun. 33, 885 (1980).

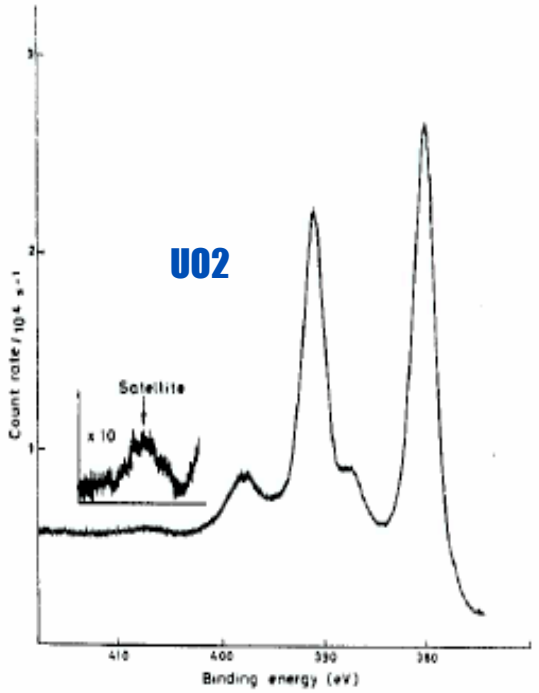
Pioneering Work- XPS of UO_2 by Allen, Trickle and Tucker



The U 4d region, recorded using monochromatized Al Kα X-rays for the clean U surface (A) and the oxidized (UO_2) surface (B).

← The satellites in the U4d of UO2 are not present in the U4d features of U.

The U4f satellites in UO2 include both a 6-eV and a 12-eV peak. →

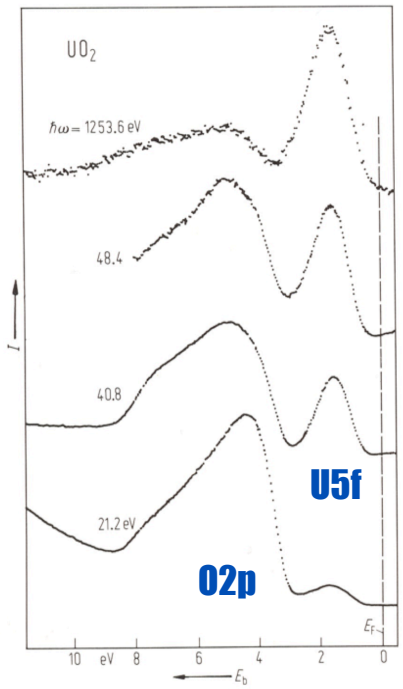


The U 4f region recorded for the oxidized (UO_2) surface of U.

- G.C. Allen, I.R. Trickle and P.M. Tucker, Philos. Mag. B 43, 689 (1981).

Pioneering Work-XPS and UPS of Uranium Oxides

Dependence of the O2p and U5f upon hv and concentration



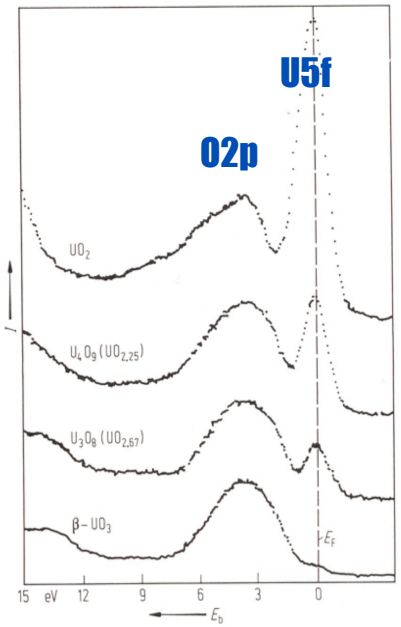


Fig. 115. UO_x. Valence band XPS spectra ($\hbar\omega$ = 1486.6 eV) of several uranium oxides. The U(5f) peak near E_F is attenuated with increasing uranium oxidation [76T, 82G]. See also [74V2].

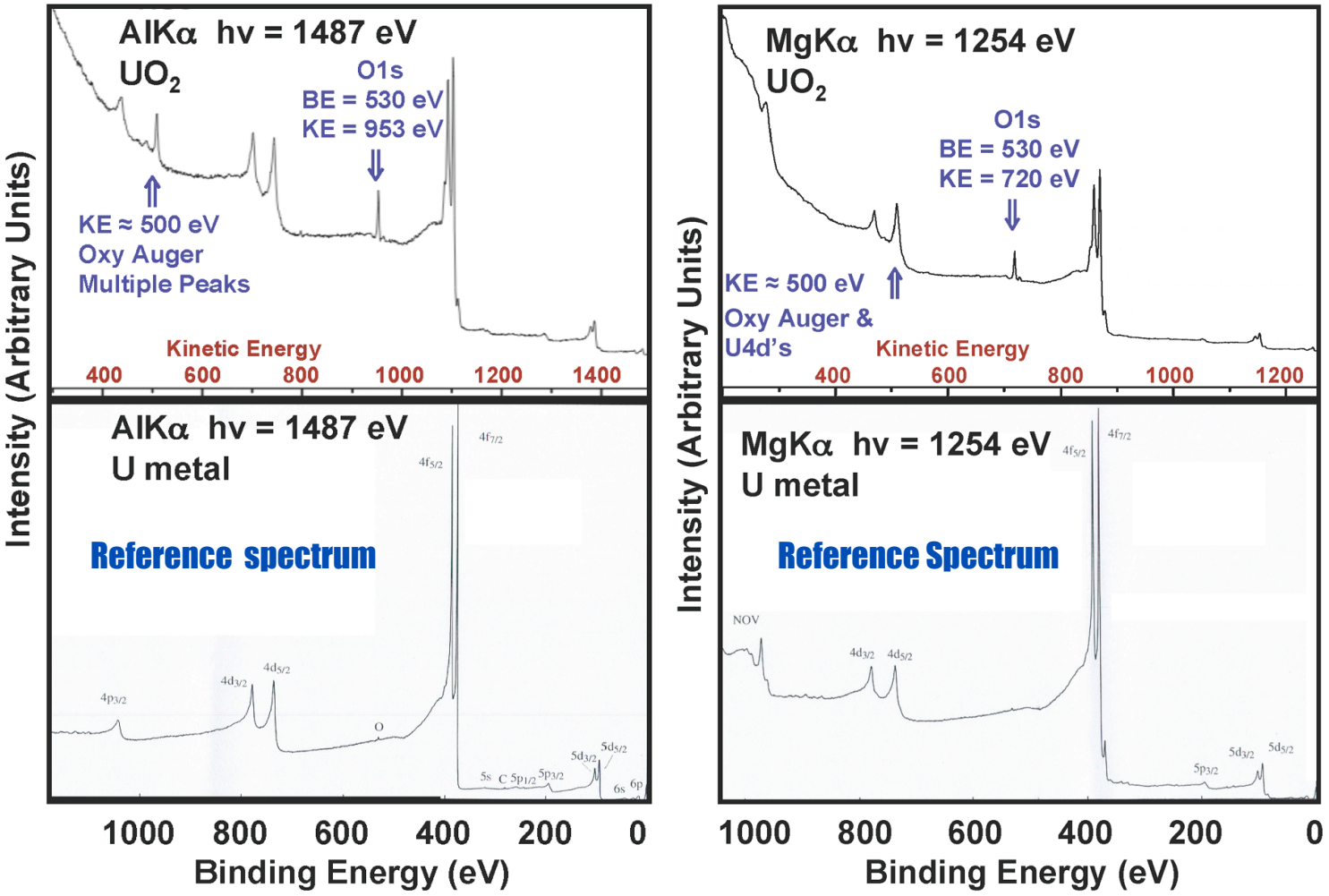
◀

Fig. 116. UO_2. Photoelectron spectra recorded for different photon energies [85N1]. E_b relative to E_F. Similar results by [77E].

Landolt-Börnstein
New Series III/23b

- These striking results go back to Thibaut et al, 1976, Gmelin Handbook 1982, Naegele et al, 1985, Evans 1977, & Veal and Lam 1974.
- J. R. Naegele, *Actinides and some of their alloys and compounds*, Electronic Structure of Solids: Photoemission Spectra and Related Data, Landolt-Bornstein *Numerical Data and Functional Relationships in Science and Technology*, ed. A Goldmann, Group III, Volume 23b, Pages 183 - 327 (1994).

What can we get from XPS? Sample composition! Example: UO_2-Nothing there but U and Oxygen

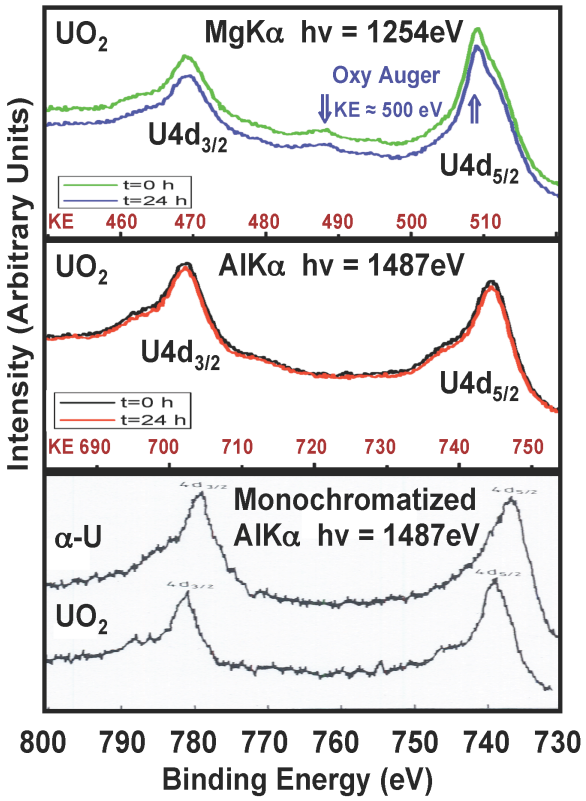


We made a UO_2 sample in a particularly simple way and needed to prove that it was actually UO_2.

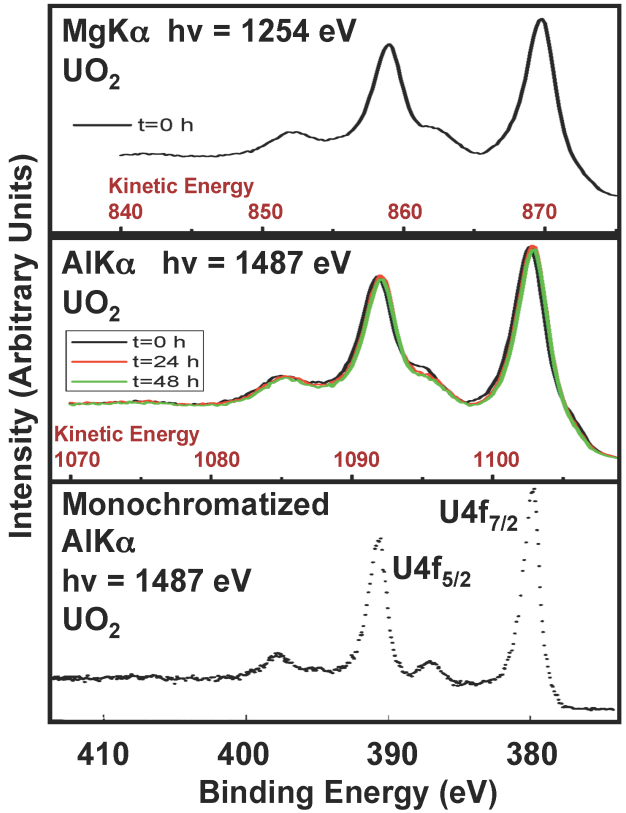
Yu and Tobin, JVSTA 29, 021008 (2011).

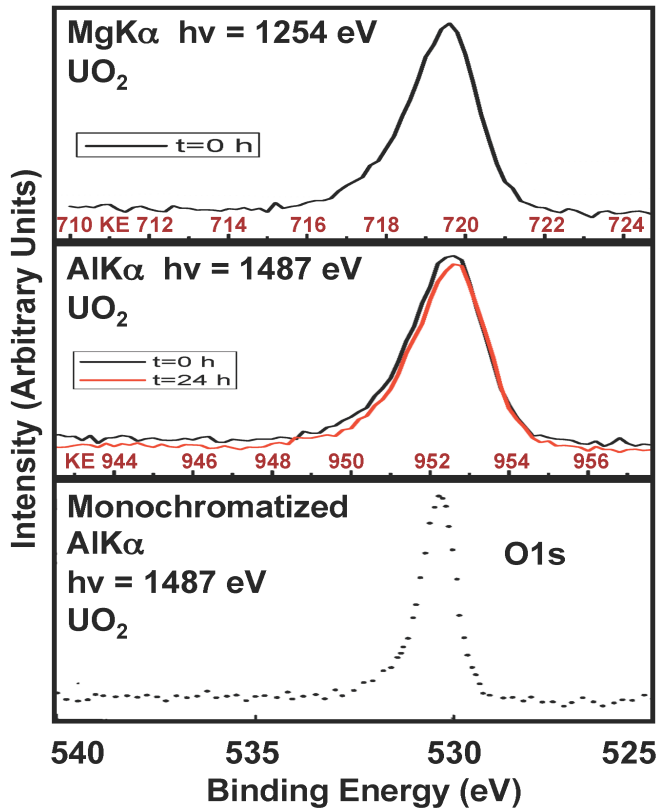
Reference spectra from Phi handbook.

What can we get from XPS?
Sample purity & a beginning on stoichiometry



Compared to Allen, Trickle & Tucker



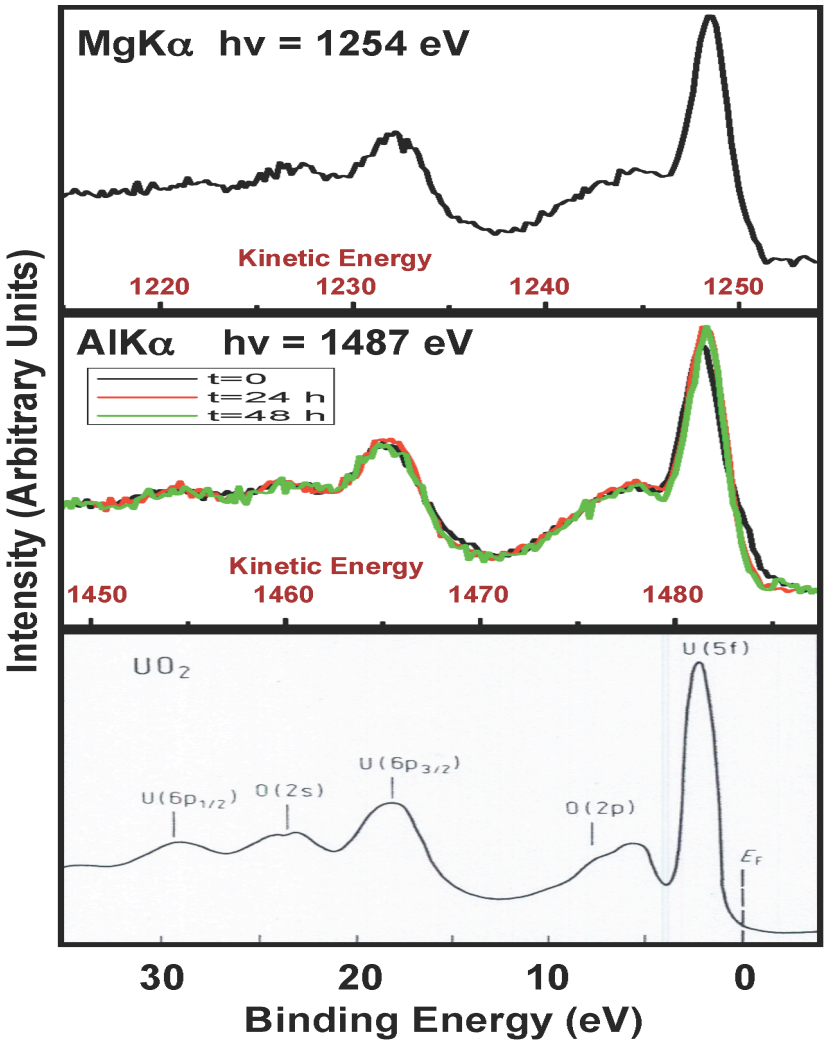


Compared to Baer & Schoenes, high res

Satellite structure agrees with UO2 not U; one Oxy site!

What can we get from XPS?

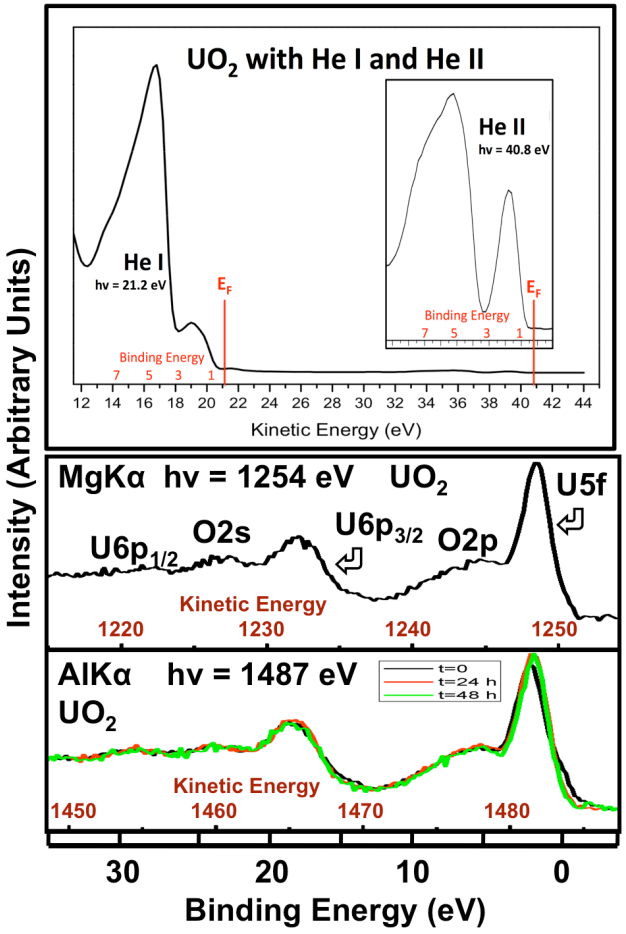
From the valence bands, we can get the elemental origins of the components and confirm that we agree with previous results…



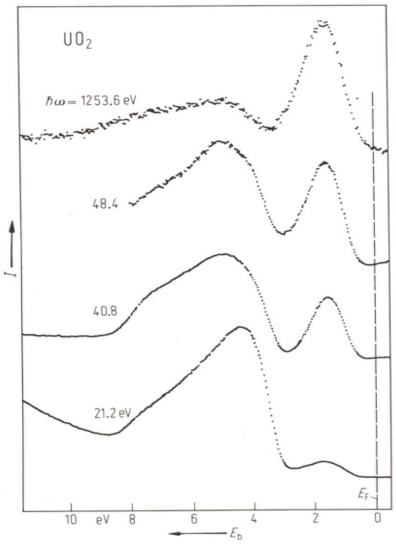
Our AlKα and MgKα spectra agree completely with the earlier result for UO2 from Veal and Lam, down to the shape of the spectrum!

B.W. Veal and D.J. Lam, Phys. Rev. B 10, 4902 (1974) and Phys. Letters 49A, 466 (1974).

What can we get from XPS and UPS? The detailed stoichiometry!



We understand the variation of O2p and U5f intensities with hv as being due to cross section effects.



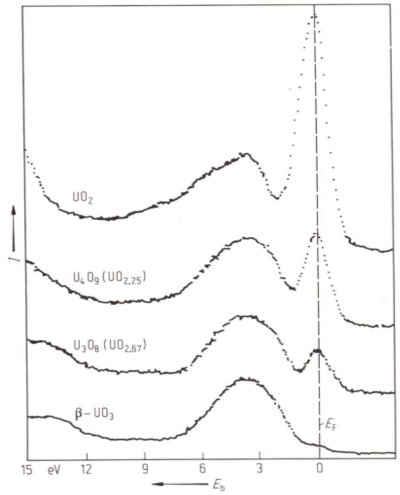


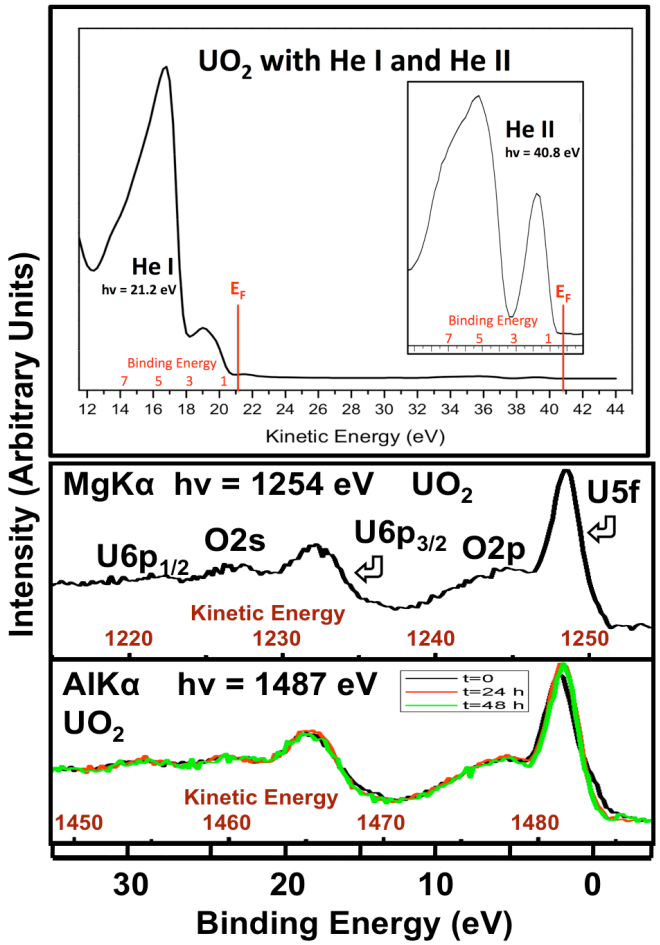
Fig. 115. UO_x. Valence band XPS spectra ($\hbar\omega$ = 1486.6 eV) of several uranium oxides. The U(5f) peak near E_F is attenuated with increasing uranium oxidation [76T, 82G]. See also [74V2].

Fig. 116. UO_2. Photoelectron spectra recorded for different photon energies [85N1]. E_b relative to E_F. Similar results by [77E].

- From comparison with these results in Naegele's review, it is clear that we have UO2, not U4O9, nor U3O8, nor UO3.
- The UPS (He I and He II) results confirm the analysis.

XPS and UPS confirm that we have a pure $UO_{2\pm x}$ sample, with small x, with a measure of the occupied density of states

UPS and XPS of UO_2



- **The assignments here go back to Veal and Lam (1974) and are supported by other workers as well.**
- **B.W. Veal and D.J. Lam, Phys. Rev. B 10, 4902 (1974) and Phys. Letters 49A, 466 (1974).**
- **J.R. Naegele, "Actinides and Some of their Alloys and Compounds," Electronic Structure of Solids: Photoemission Spectra and Related Data, Landolt-Bornstein "Numerical Data and Functional Relationships in Science and Technology," ed. A Goldmann, Group III, Volume 23b, Pages 183 – 327 (1994).**
- **For the complete UPS and XPS study, see Yu and Tobin, JVSTA 29, 021008 (2011).**

Pioneering Work on Transuranics by Naegele et al

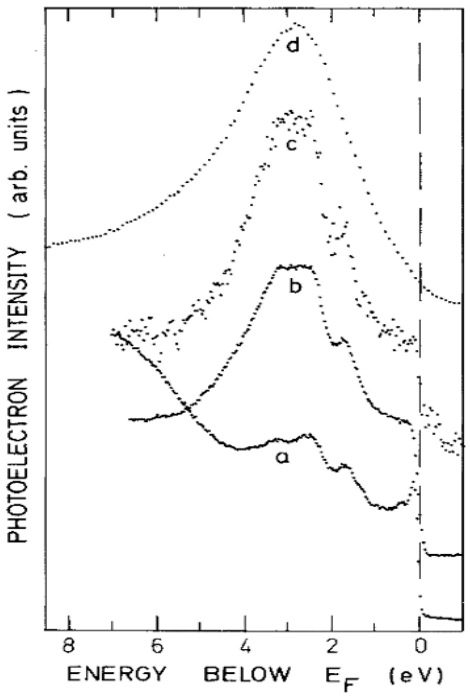


FIG. 1. UPS/XPS conduction-band spectra of Am metal for (a) 21.1, (b) 40.8, (c) 48.4, and (d) 1253.6 eV excitation energy.

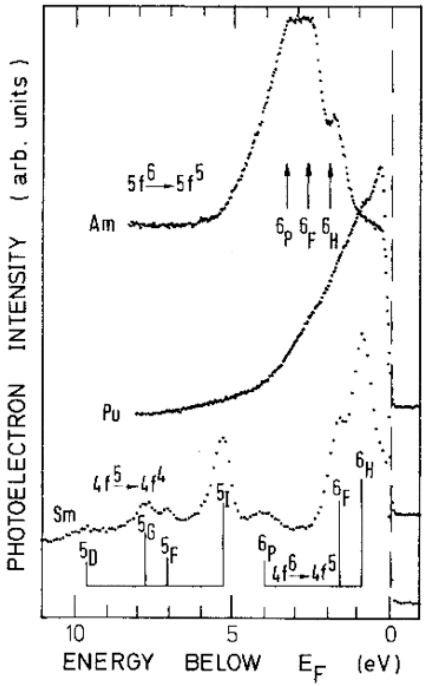


FIG. 2. Conduction-band spectra of Am, Pu, and Sm metal for 40.8-eV excitation.

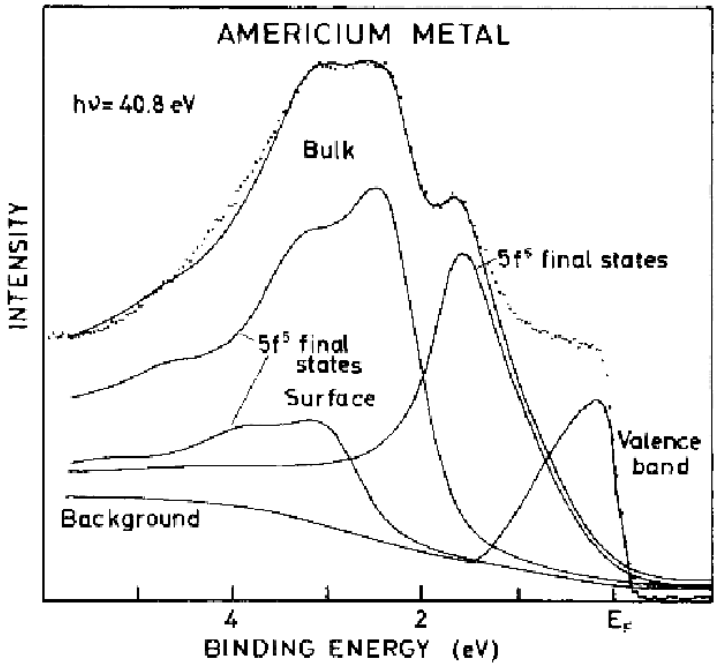


FIG. 1. The He II—excited photoelectron spectrum from Am metal is analyzed in terms of two shifted and broadened $5f^5$ final-state multiplets representing bulk and surface emission, respectively, and a broadened $5f^6$ final-state structure (see text). Subtraction of these contributions yields a 1.5-eV broad feature at E_F which is interpreted as the Am d-band emission. The inelastic background is assumed to be proportional to the integrated intensity at higher kinetic energies.

- **J. R. Naegele, L. Manes, J. C. Spirlet, and W. Müller, Phys. Rev. Lett. 52, 1834 (1984);**
- **N. Martensson, B. Johansson, and J. R. Naegele, Phys. Rev. B 35, 1437 (1987).**

An example of more recent work on transuranics at ITU: triplet structure in the Pu 5f's in compounds

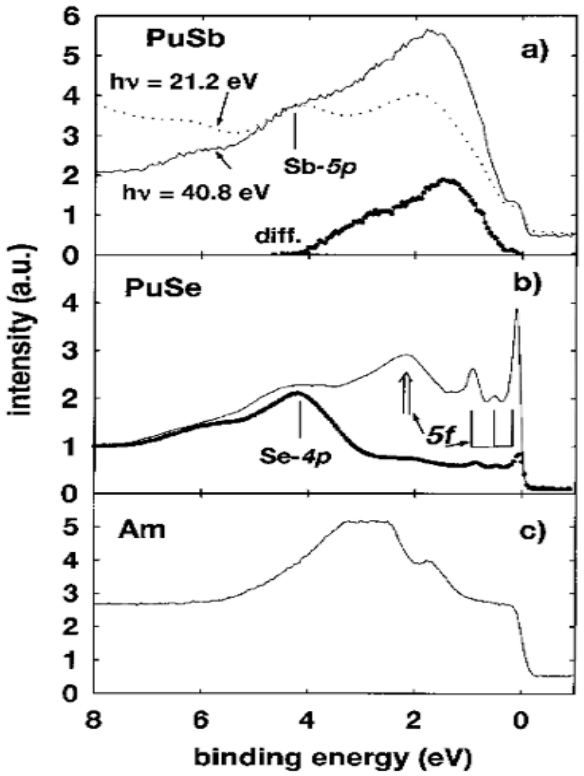


FIG. 2. UPS valence-band spectra. For PuSb (a), the full line represents the spectrum with $h\nu = 40.8$ eV, the dotted line the spectrum with $h\nu = 21.2$ eV; full circles represent the difference spectrum. For higher binding energies than 5 eV, the difference spectrum is negative due to the higher secondary-electron background for $h\nu = 21.2$ eV in this energy range. For PuSe (b) the spectrum taken with $h\nu = 40.8$ eV photon energy is represented by the full line, for $h\nu = 21.2$ eV by full circles. For Am (c), only the spectrum with $h\nu = 40.8$ eV is displayed (data taken from Ref. [2]).

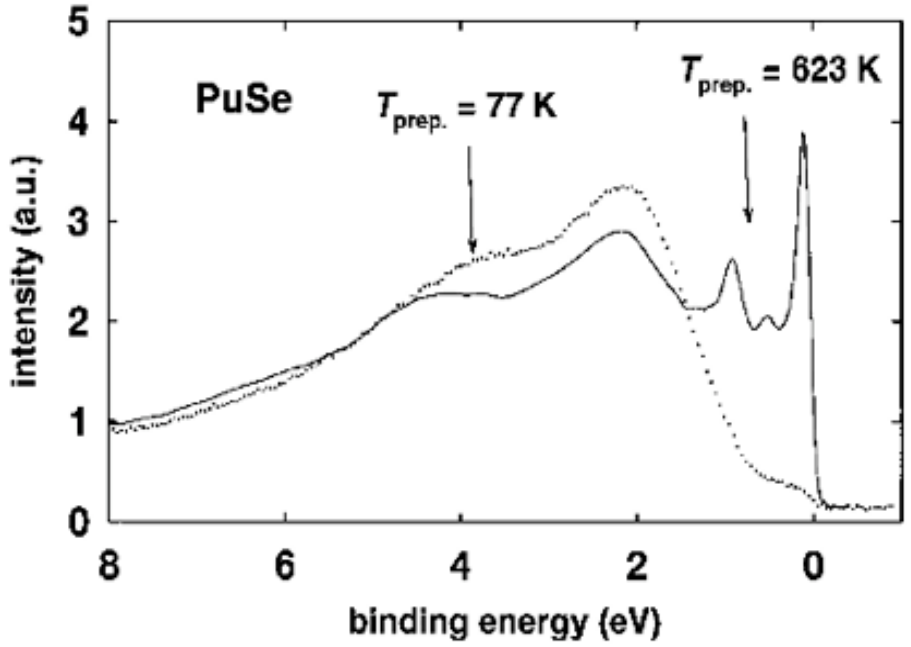


FIG. 3. UPS valence-band spectra (taken at $h\nu = 40.8$ eV photon energy) of PuSe layers deposited at $T = 623$ K (full line) and 77 K (dotted line).

- **T. Gouder, F. Wastin, J. Rebizant, and L. Havela, Phys. Rev. Lett. 84, 3378 (2000).**

An example of more recent work on transuranics at ITU: triplet structure in the Pu 5f's as a function of coverage

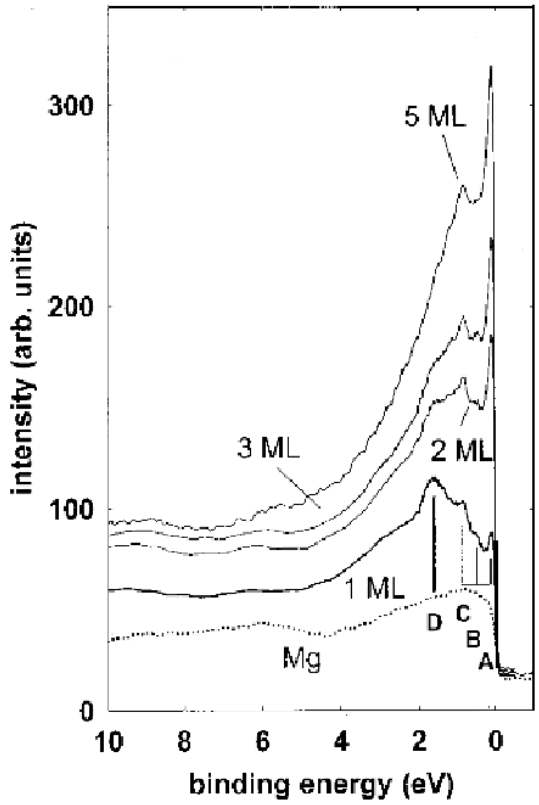


FIG. 4. Valence-band spectra of pure Mg substrate and increasing coverage of Pu. The thickness is indicated in the number of monolayers. Spectra were obtained with the photon energy $h\nu = 40.8$ eV. The vertical bars indicate the position of the $5f$-localized peak and the triplet of narrow features, described in the text.

- **This is quite intriguing: one can watch the development of the triplet structure as a function of deposition.**
- **While the growth mode is unknown, it is clear that the electronic structure has converged to the bulk limit by 5 ML.**
- **L. Havela, T. Gouder, F. Wastin, and J. Rebizant, Phys. Rev. B 65, 235118 (2002)**

In house work on transuranics at LANL: PuCoGa5, the Pu superconductor

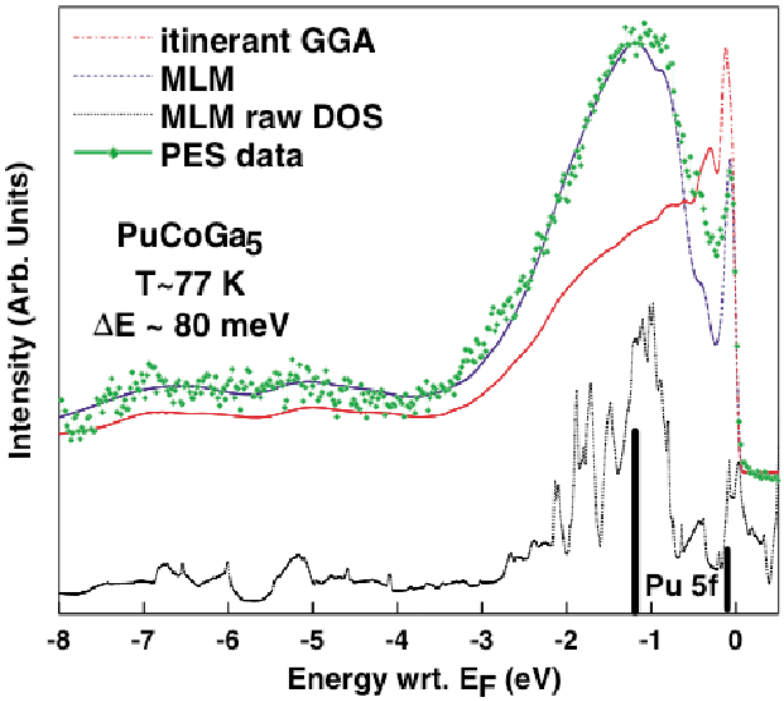
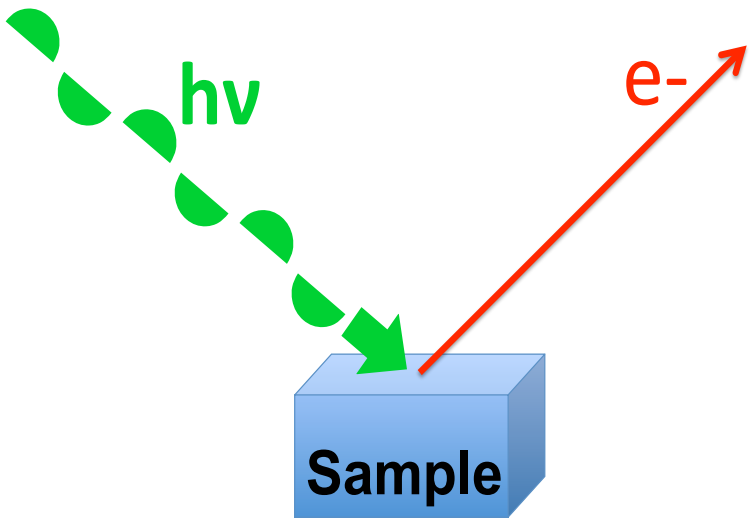


FIG. 2 (color online). The photoemission data for $PuCoGa_5$ is compared against model calculations. The experimental valance band PES data is shown as diamonds, a GGA calculation as a dot-dashed line, a MLM calculation as a dashed line, and a raw MLM DOS as a dotted line (f-electron postion centers are represented by solid bars). The calculations (less the raw DOS) have been processed for photohole lifetime, instrument, and Fermi function broadening.

- **This impressive measurement was taken at LANL, using a He lamp.**
- **Clearly, there is a persistence of Pu 5f states in the Pu-SC.**
- **J. J. Joyce, J. M. Wills, T. Durakiewicz, M. T. Butterfield, E. Guziewicz, J. L. Sarrao, L. A. Morales, A. J. Arko, and O. Eriksson, Phys. Rev. Lett. 91, 176401 (2003)**

Synchrotron-radiation-based photoelectron spectroscopy (PES), including Resonant PES or RESPES



Select energy (and direction) of electrons

Tunable hv source

Thus, double monochromatization: Both hv and electrons.

$$h\nu = KE_e + B^F + \Phi$$

Pioneering Work- Arko et al
5f Dispersion in Uranium Compounds

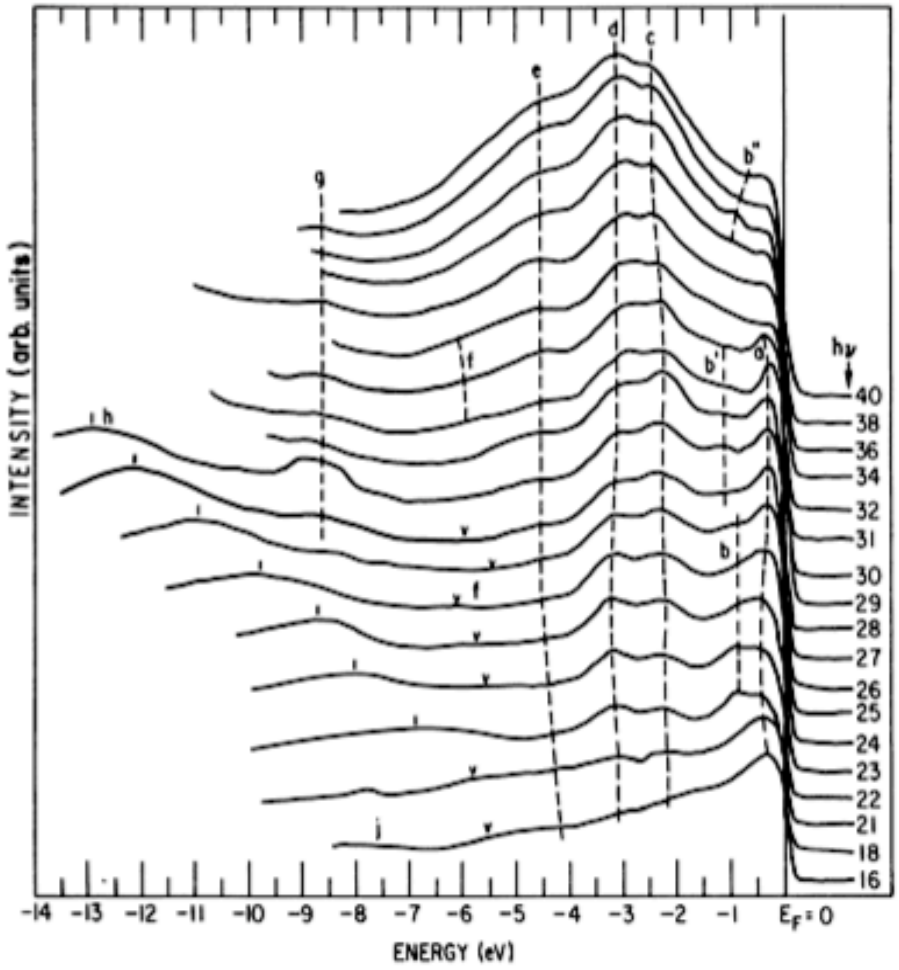


FIG. 5. Normal-emission EDC's for a $UIr_3(100)$ surface. Feature *g* is a surface impurity. Feature *h* (denoted by tic marks) is due to a final-state critical point at ~14 eV.

- Before, we were not concerned about the direction of the emitted electrons.
- Now, the energy selection and direction specification of the electrons will permit a momentum analysis.
- The tunability of synchrotron radiation allows mapping of Eenergy vs k along the surface normal, which is often the "cleanest" measurement.
- When coupled with a single crystal, this means one can band-map, i.e determine the energy vs k relationships of the occupied electronic states, the valence bands.
- Arko, Koelling and Reihl, PRB 27, 3955 (1983)

The bandmapping studies are being continued by workers at LANL, using the facilities at the UWSRC

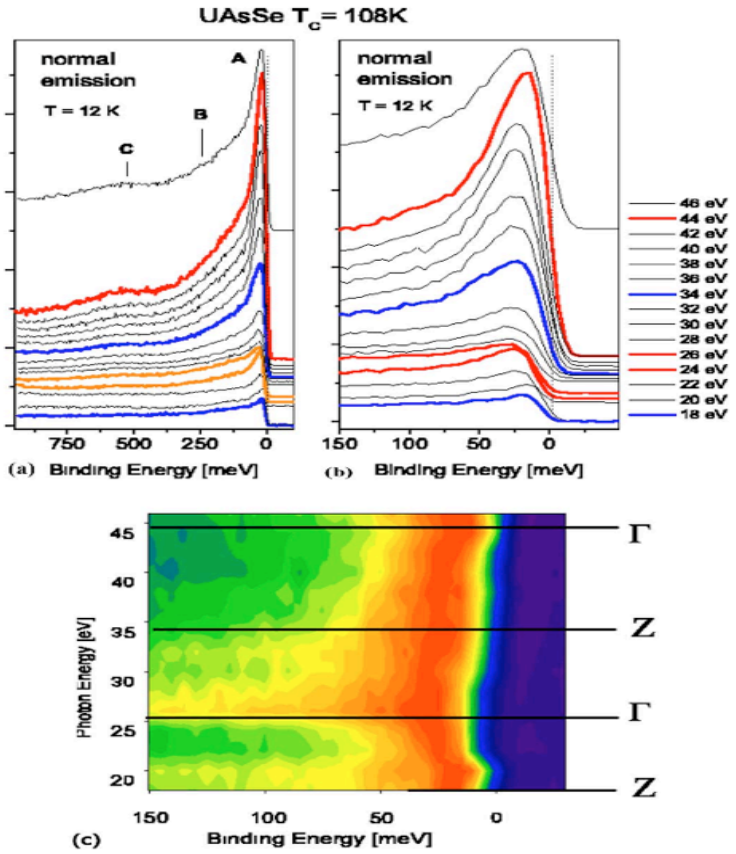


FIG. 4. (Color online) Normal-emission ARPES of UAsSe (Γ -Z direction in the Brillouin zone) taken at 12 K within 950 meV (a) and 150 meV (b) of the Fermi edge. Binding energy in (c) is the same as in (b), but the intensity is normalized to the maximum. Spectra marked in red show the spectra nearest to the Γ point of the Brillouin zone whereas spectra marked in blue show the Z point of the Brillouin zone.

- Note the energy scale here: it is meV, not eV…high resolution.
- The LANL people have a vibrant program at the Univ. of Wisconsin Synchrotron Radiation Center, using in situ cleaved samples.
- E. Guziewicz, T. Durakiewicz, P. M. Oppeneer, J. J. Joyce, J. D. Thompson, C. G. Olson, M. T. Butterfield, A. Wojakowski, D. P. Moore, and A. J. Arko, Phys. Rev. B 73, 155119 (2006).

Resonant PES is another measurement enabled by the tunability of synchrotron radiation: U-RESPES

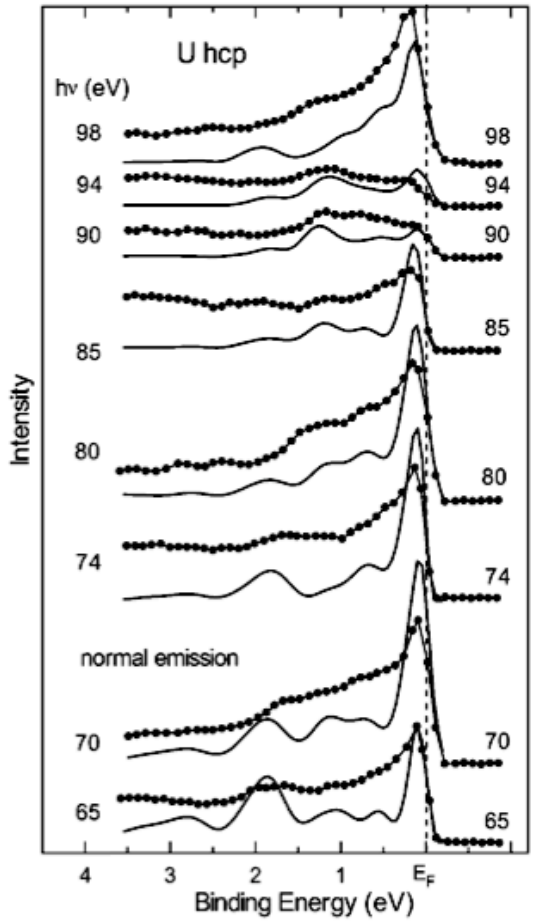


FIG. 1. Experimental valence-band PE spectra (solid lines through data points) and calculated EDC's (solid subspectra) of hcp U(0001).

- In RESPES, a second, indirect channel for photoemission, through a core level, is opened.
- It is necessary that the photon energy be sufficient to excite the core level electron out of the core level, into the lowest unoccupied states.
- There is a strong quantum mechanical quality of this event, akin to the Young's two slit problem.
- The binding energies of the members of U4d doublet are 94 eV and 102 eV.
- **Molodstov, Halilov, Richter, Zangwill and Laubschat, PRL 87, 017601 (2001)**

Pioneering Work-PES on Resonance in Uranium compounds by JW Allen et al

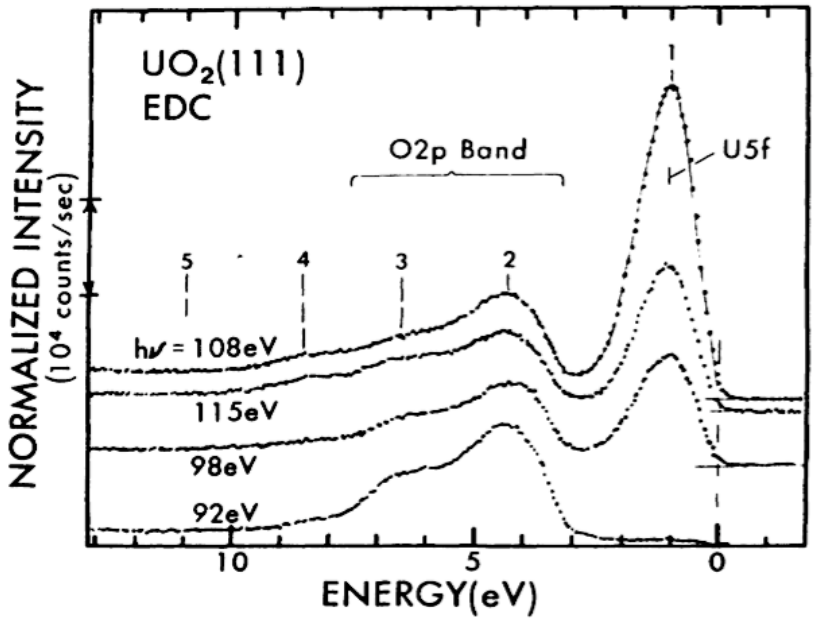


FIG. 2. Energy-distribution curves (EDC's) for the UO_2 valence band at photon energies corresponding to the Fano minimum (92 eV) and maxima (98 and 108 eV). The photon energies at which the CIS spectra shown in Fig. 3 were obtained are indicated by the numbers near the 108-eV spectrum. The 115-eV spectrum is included because of the resonant enhancement exhibited by the 8.5-eV satellite at this energy.

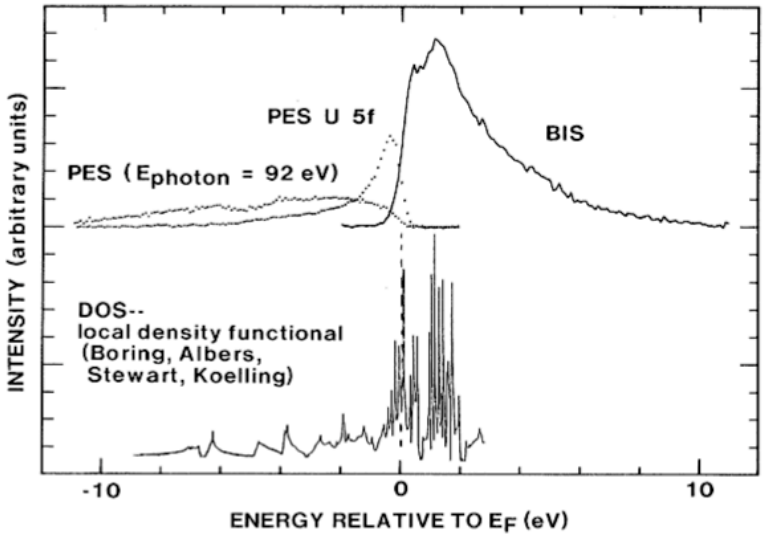
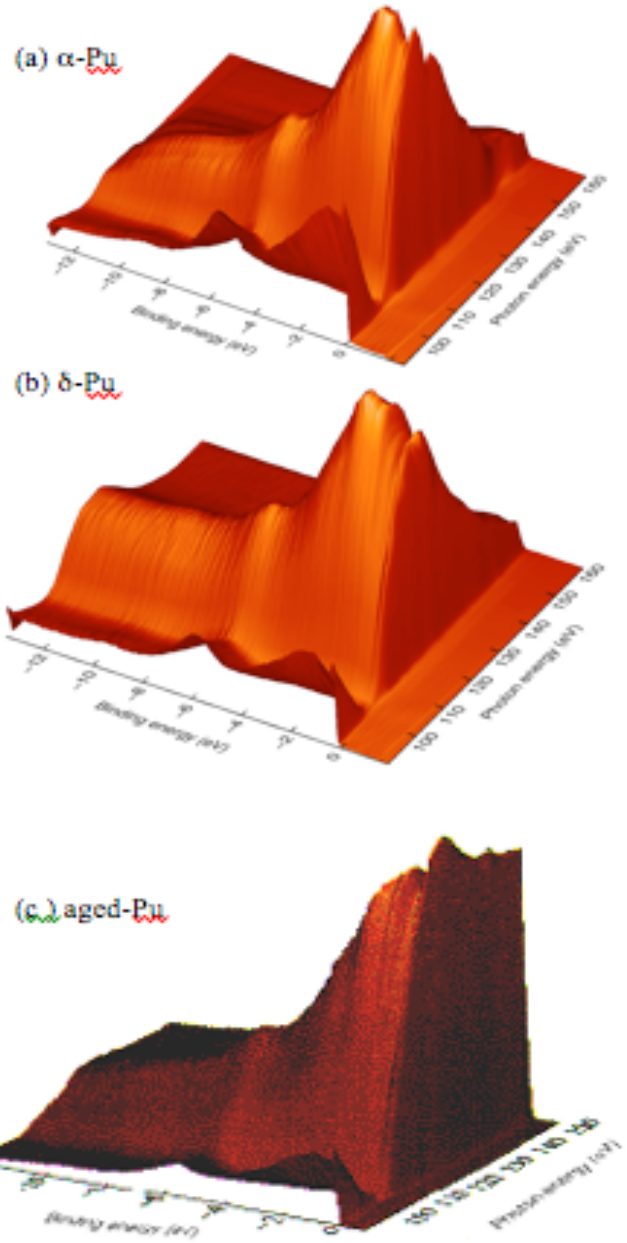


FIG. 1. Top: PES and BIS spectra for UAl_2, as described in the text. Bottom: local density-functional density of states from Ref. 14.

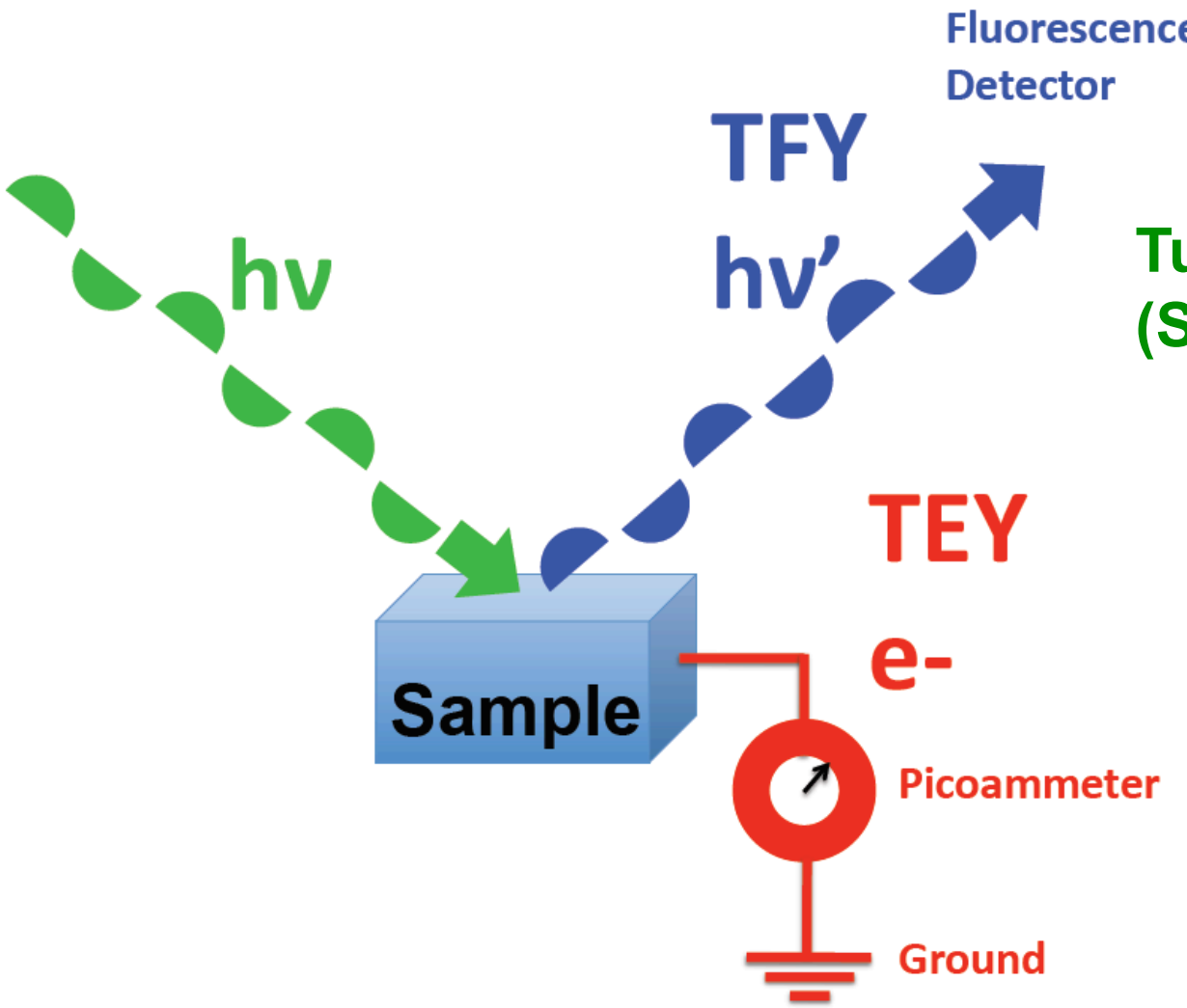
- **Allen, Oh, Cox, Ellis, Wire, Fisk, Smith, Pate, Lindau and Arko, PRL 54, 2635 (1985)**
- **Cox, Ellis, Cowan, Allen, Oh, Lindau, Pate and Arko, PRB 35, 5761 (1987)**

The only synchrotron radiation PES study of Pu-Tobin et al.

- There was a single time that Pu was probed with tunable soft x-rays at a storage ring, at the ALS in Berkeley.
- One result was the 5d RESPES of Pu: the three axes are hv, binding energy and intensity. hv was over the range of about 90 -160 eV (the binding energy of the Pu 5d is about 102 eV.)
- Clearly, there is a resonance in Pu
- J. G. Tobin, B. W. Chung, R. K. Schulze, J. Terry, J. D. Farr, D. K. Shuh, K. Heinzelman, E. Rotenberg, G. D. Waddill, and G. van der Laan, Phys. Rev. B 68, 155109 (2003)



X-ray absorption spectroscopy (XAS)



Tunable hv source (Synchrotron radiation)

Total fluorescence yield (TFY) is less surface sensitive than Total electron yield (TEY).

Pioneering Work in XAS: a digression into EELS
Moser, Delley, Schneider, and Baer

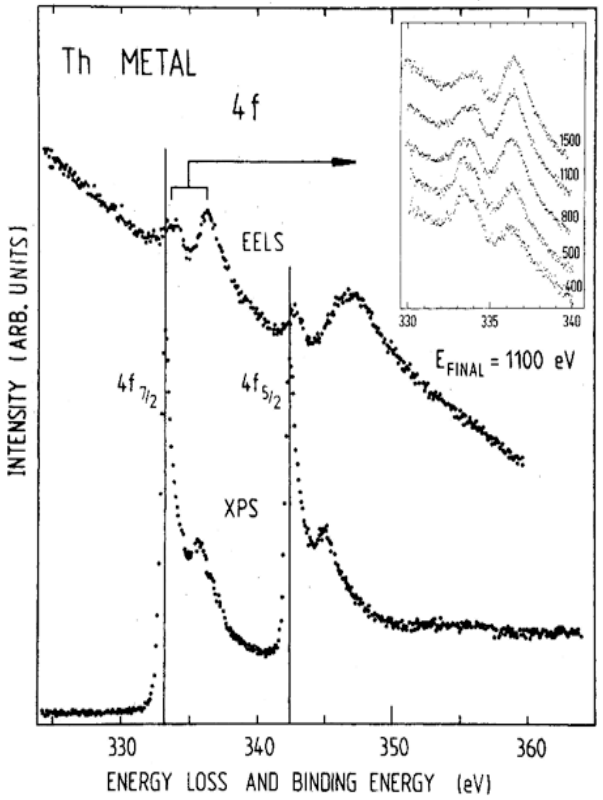


FIG. 2. EELS and XPS 4*f* core-excitation spectra of Th metal on a common energy scale. The inset shows the excitation energy dependence of the low-energy-loss structure. The common onset of the EELS and XPS edges is indicated by two parallel lines drawn through the maxima of the spin-orbit-split $4f_{7/2}$ and $4f_{5/2}$ XPS components.

At high enough energies, Electron Energy Loss becomes equivalent with XAS.

Although this is not XAS, it is close …

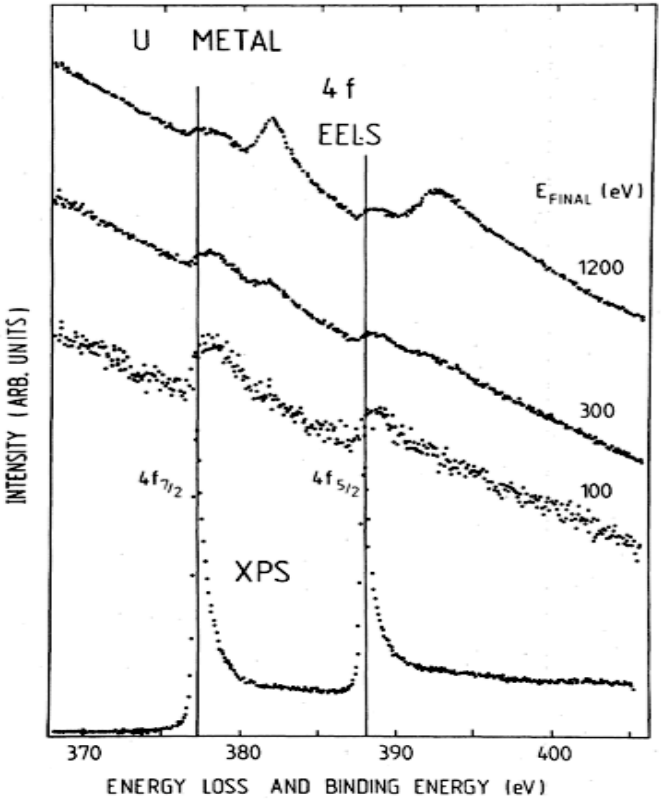


FIG. 3. EELS spectra, taken at the indicated final-state energies, and XPS 4*f* core-excitation spectra of U metal. The common onset of the EELS and XPS emission is indicated by the two parallel lines drawn through the maxima of the spin-orbit-split XPS components.

H. R. Moser, B. Delley, W. D. Schneider, and Y. Baer, Phys. Rev. B 29, 2947 (1984)

Pioneering Work: XAS of U compounds by Kalkowski, Kaindl, Brewer, and Krone

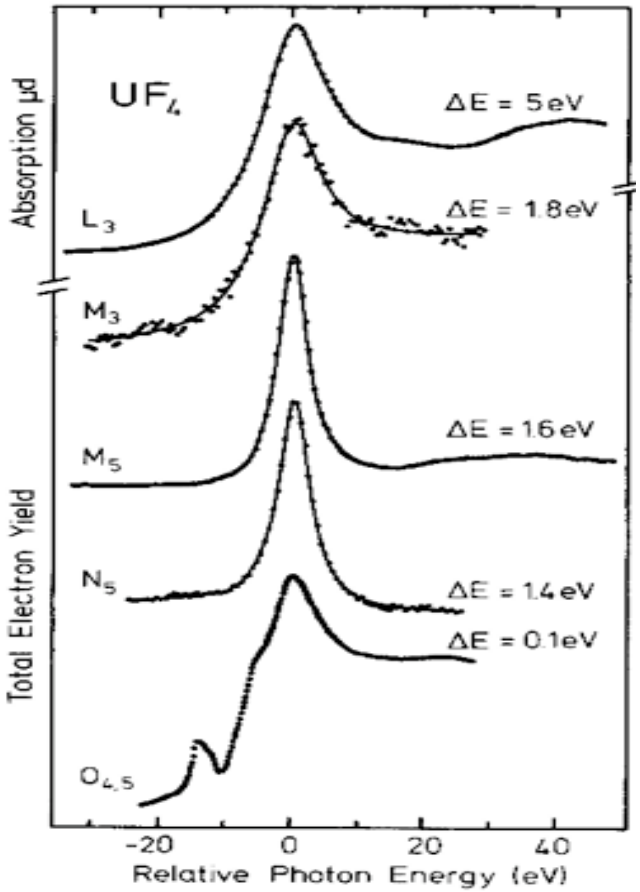


FIG. 1. Near-edge XA fine-structure spectra of UF_4 at the L_3, M_3, M_5, N_5, and $O_{4,5}$ thresholds, which are located at photon energies of about 17 180, 4310, 3550, 730, and 110 eV, respectively. For each spectrum the energy resolution ΔE (FWHM) of the employed monochromator is given.

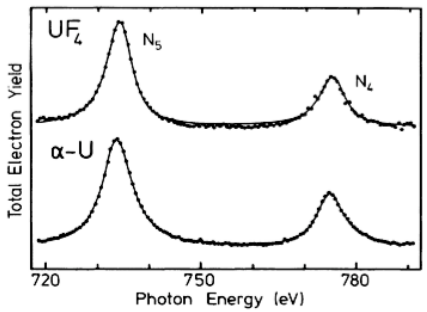


FIG. 7. Total-electron-yield spectra of α-U metal and UF_4 at the $N_{4,5}$ thresholds. The solid lines represent fit results.

This is beautiful work!

G. Kalkowski, G. Kaindl, W. D. Brewer, and W. Krone, Phys. Rev. B 35, 2667 (1987)

TEY only

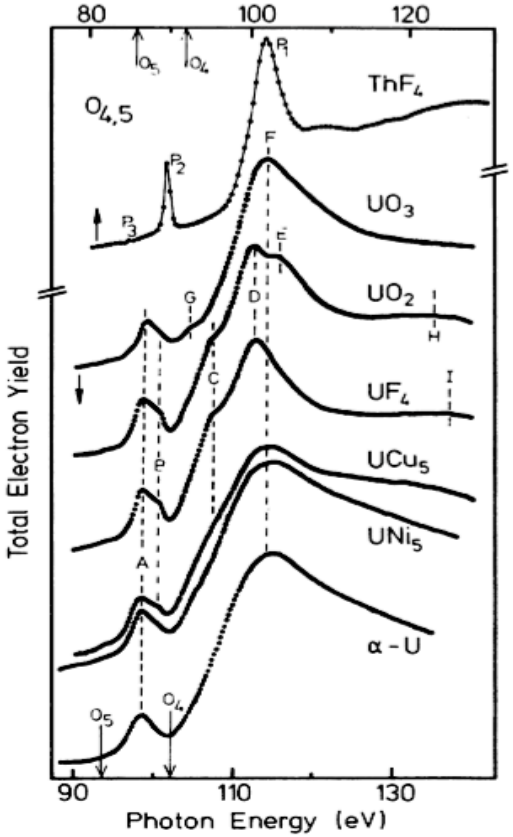


FIG. 8. Total-electron-yield spectra of various U compounds and of ThF_4 at the $O_{4,5}$ thresholds. Note the different energy scales for the Th and U spectra; the arrows specify the O_4 and O_5 thresholds from XPS measurements of Th and α-U metal, respectively (Ref. 46). The various spectral features are explained in the text. The solid lines through the data points serve as guides to the eye.

In uranium compounds, the other elements were also pursued: e.g. O1s XAS of UO2

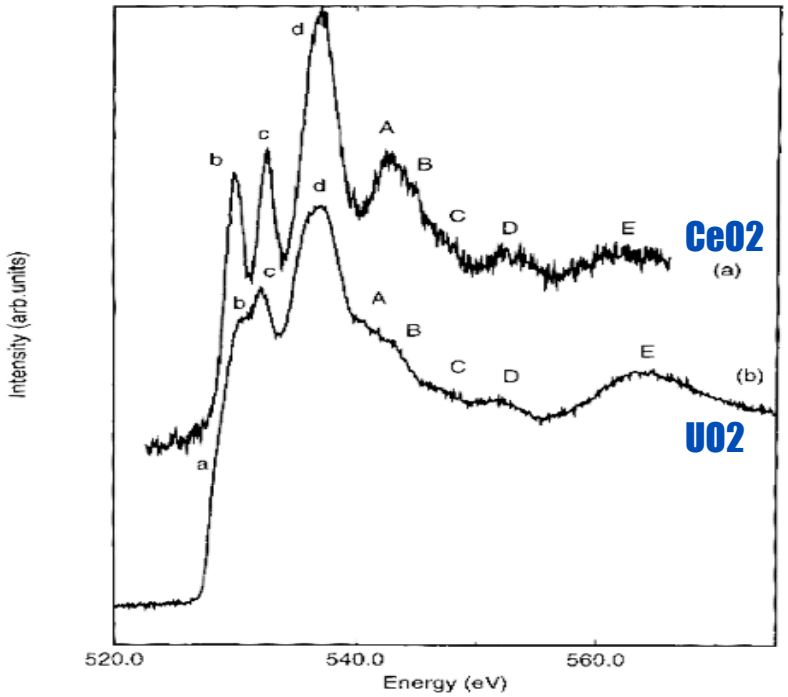


Figure 1. XAS oxygen K edge of CeO_2 (a) and UO_2 (b).

Table 1. Energies of the structures of the O K XAS spectrum for CeO_2 and UO_2.

	a	b	c	d	A	B	C	D	E
CeO_2 (eV)	—	530.9	533.5	537.9	543.6	545.7	548.7	553.9	563.4
UO_2 (eV)	528.55	530.65	532.2	537.0	540.9	543.1	546.85	551.85	564.05

- **These were TEY measurements, coupled to theory.**
- **F. Jollet, T. Petit, S. Gota, N. Thromat, M. Gautier-Soyer, and A. Pasturel, J. Phys.: Condens. Matter. 9, 9393 (1997).**

XAS, EELS and Simulations for the 4d edges of Pu by Tobin et al

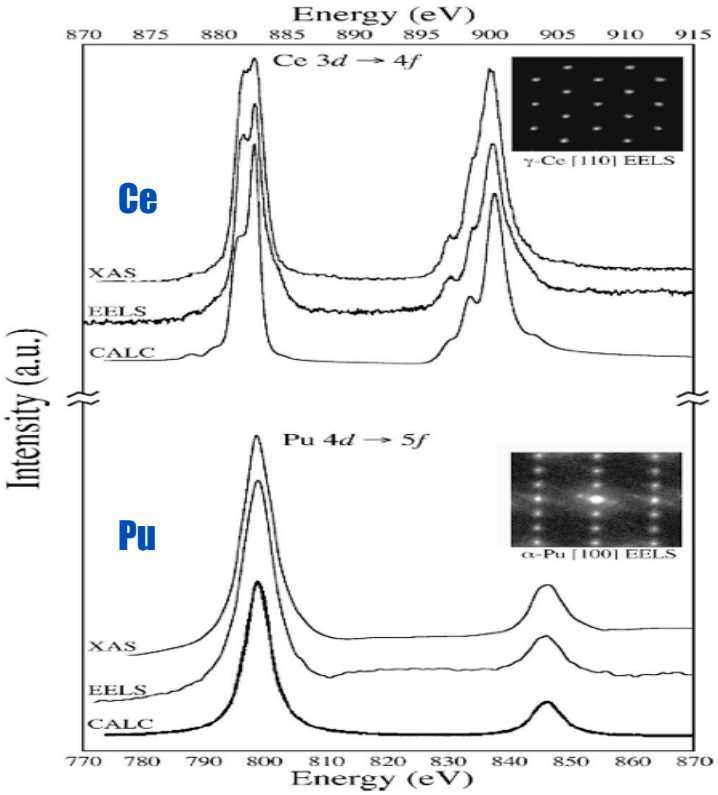


FIG. 2. White line spectra α-Pu ($N_{4,5}, 4d \rightarrow 5f$) and Ce ($M_{4,5}, 3d \rightarrow 4f$) acquired by EELS in a TEM, XAS, and spectral simulation are shown here. A single-crystal diffraction pattern from each metal is presented, confirming the phase being examined by EELS. For Ce, the $3d_{5/2}$ peak is near 884 eV and the $3d_{3/2}$ peak is near 902 eV. For Pu, the $4d_{5/2}$ peak is near 798 eV and the $4d_{3/2}$ peak is near 845 eV (Ref. 14). Note the significantly different energy scales for Ce and Pu.

- The XAS is from the same study as the RESPES of Pu
- At high enough energies, EELS becomes equivalent with XAS
- The theory was by G. van der Laan.
- J. G. Tobin, K. T. Moore, B. W. Chung, M. A. Wall, A. J. Schwartz, G. van der Laan, and A. L. Kutepov, Phys. Rev. B 72, 085109 (2005).

The ALS Group is pushing into transuranics using very small samples to minimize their activity

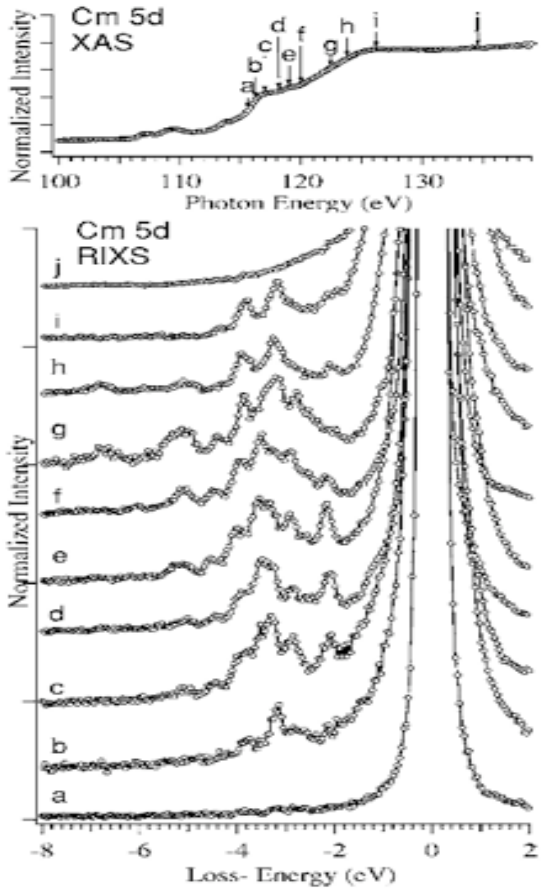
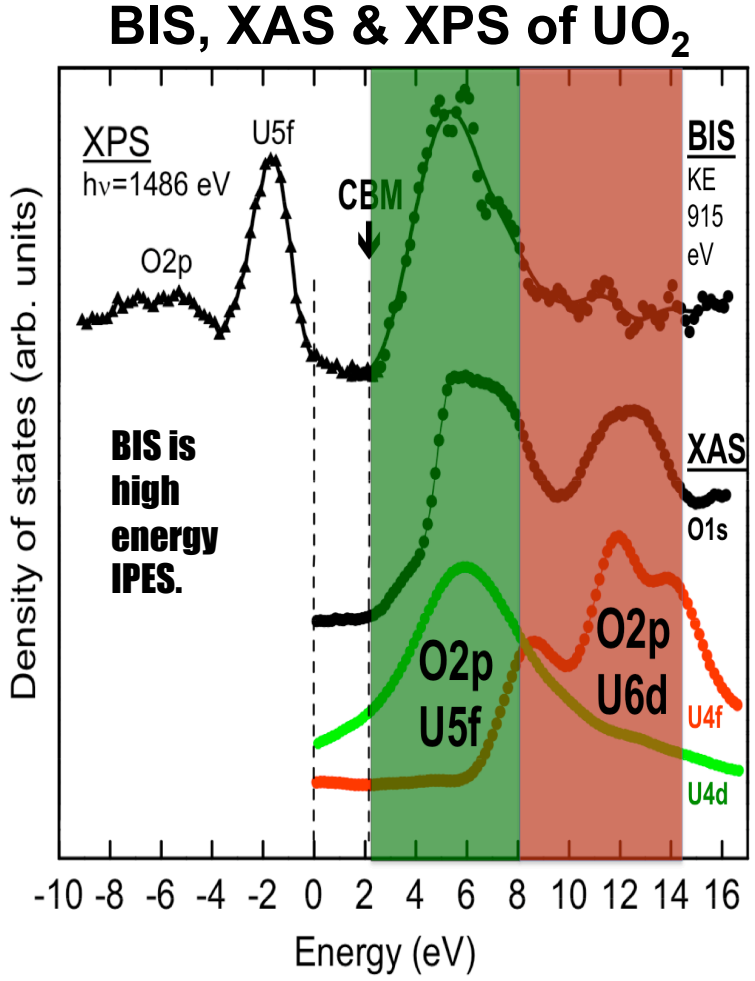


FIG. 1. Cm 5*d* XAS (top panel) and RIXS spectra across the 5*d* edge plotted on the energy-loss scale. The elastic peak is set to 0 eV. Excitations energies *a-l* are indicated by lettered arrows on the XA spectrum.

- **Here is some XAS and Resonant Inelastic X-ray Scattering (RIXS) of Cm from the ALS.**
- **This thrust builds upon the ALS expertise in micro-spectroscopy.**
- **K. O. Kvashnina, S. M. Butorin, D. K. Shuh, J.-H. Guo, L. Werme, and J. Nordgren, Phys. Rev. B 75, 115107 (2007)**

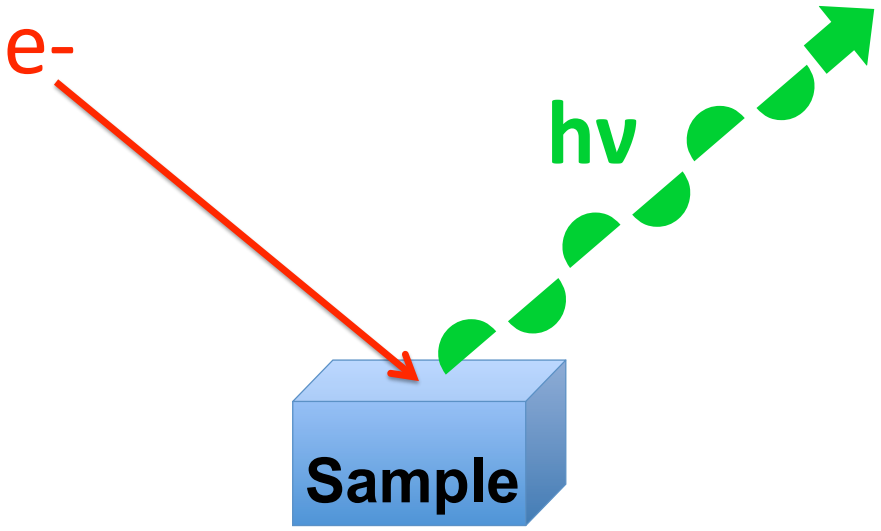
Can anything new be learned from XAS on systems such as UO2? Yes, but you'll have to wait …



- The whole can be greater than the sum of the parts…
- The Conduction Bands can be separated experimentally into U5f-O2p and U6d-O2p parts!
- This will be discussed next week, at the JdA
- S.-W. Yu, J.G. Tobin, J. C. Crowhurst, S. Sharma, J. K. Dewhurst, P. Olalde-Velasco, W. L. Yang, W. J. Siekhaus, "*f - f origin of the insulating state in uranium dioxide: X-ray absorption experiments and* first-principles calculations," Phys. Rev. B 83 xxxxxx (2011).

Inverse Photoelectron Spectroscopy (IPES, usually low energy), including Bremstrahlung Isochromat Spectroscopy (BIS, high energy) and Resonant IPES or RIPES

Mono-energetic beam of electrons



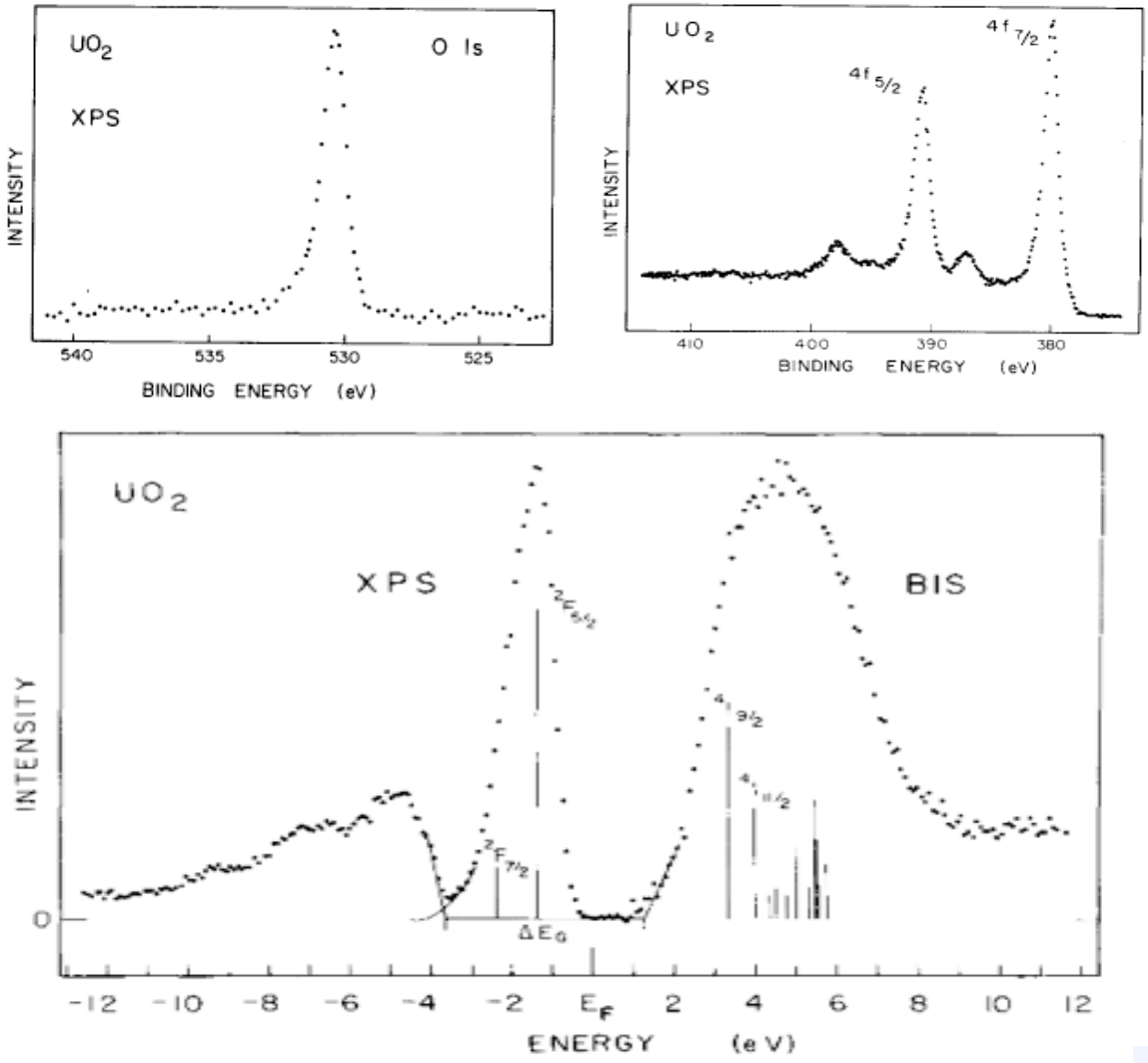
Wavelength selection in detection of hν

Can also do XES with photon in & photon out

IPES/BIS $h\nu = KE_e - H^F + \Phi$

XES $KE_e > BE\ (core)$ & $h\nu \approx BE\ (core)$

Pioneering Work-BIS and XPS of Baer and Schoenes This was so important, it had to go in twice…



- The XPS was high resolution, using monochromatized AlKα (1487eV)
- The XPS is done by running the XPS machine backwards, therefore it is at the AlKα energy
- Y. Baer and J. Schoenes, Solid State Commun. 33, 885 (1980).

Pioneering Work: BIS of Thorium and Uranium by Baer and Lang

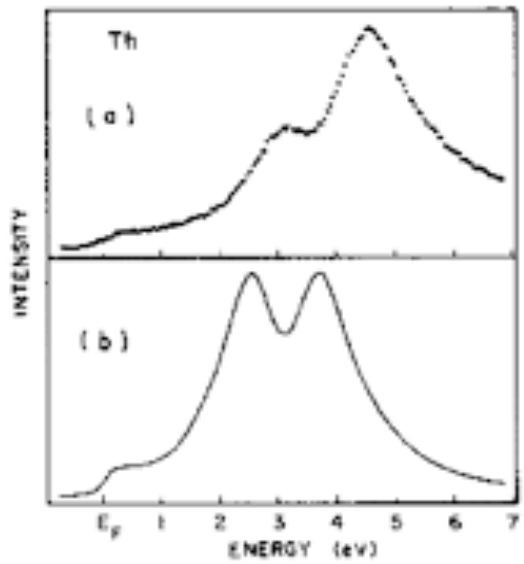


FIG. 2. BIS spectrum of Th, (a), compared to the convoluted (Ref. 22) $l=3$ projected DOS of Ref. 12, (b).

Experiment

Simulations

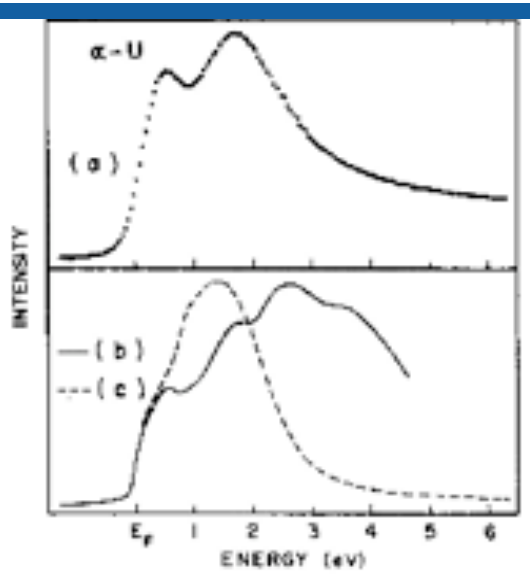


FIG. 4. BIS spectrum of U, (a), compared to the convoluted (Ref. 22) $l=3$ projected DOS of Ref. 10, (b), and of Ref. 13, (c).

- This is beautiful work, that we've quoted many times.
- We argue that the doublet structure is indicative of the spin- orbit splitting in the U5f's and Th5f's.
- Y. Baer and J. K. Lang, Phys. Rev. B 21, 2060 (1980).

Pioneering Work: IPES of UO2 by Chauvet and Baptist

- Their result is consistent with the BIS of Baer and Schoenes.
- This work was done at photon energies of 20.6, 25.3, 31 and 49.6 eV.
- Next week, I'll claim that the large peak near 4 eV is the U5f and the small one near 10 eV is the U6d.
- G. Chauvet and R. Baptist, Solid State Communications 43, 793 (1982).

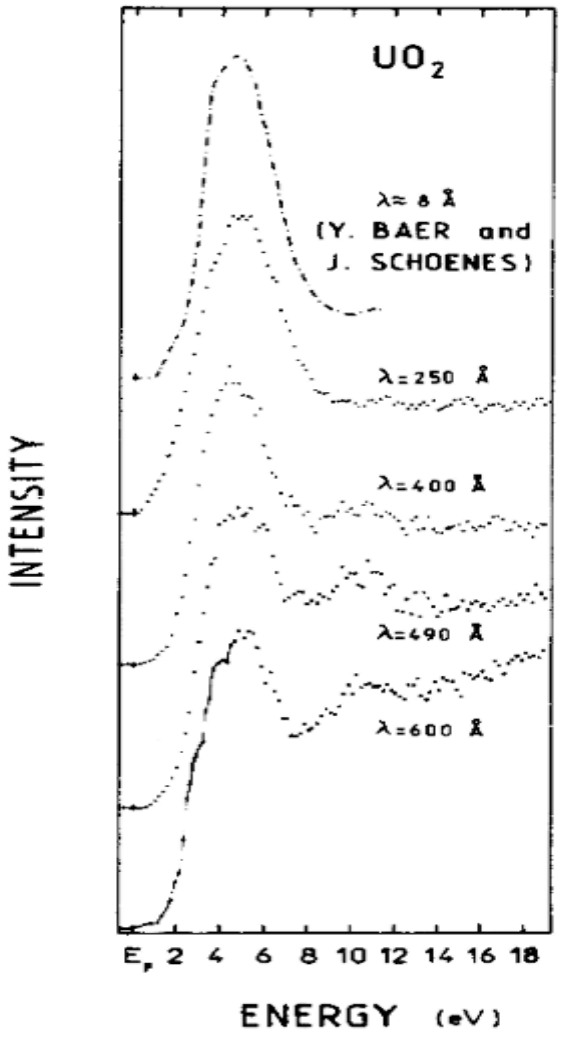


Fig. 1 – IPE spectra of UO_2 thin films recorded at : λ = 8 Å Energy ∿ 1.5 keV
λ = 250 Å Energy ∿ 49.6 eV
λ = 400 Å Energy ∿ 31 eV
λ = 490 Å Energy ∿ 25.3 eV
λ = 600 Å Energy ∿ 20.6 eV

Some more recent IPES on UO2 at AWE by Roussel, Morral and Tull

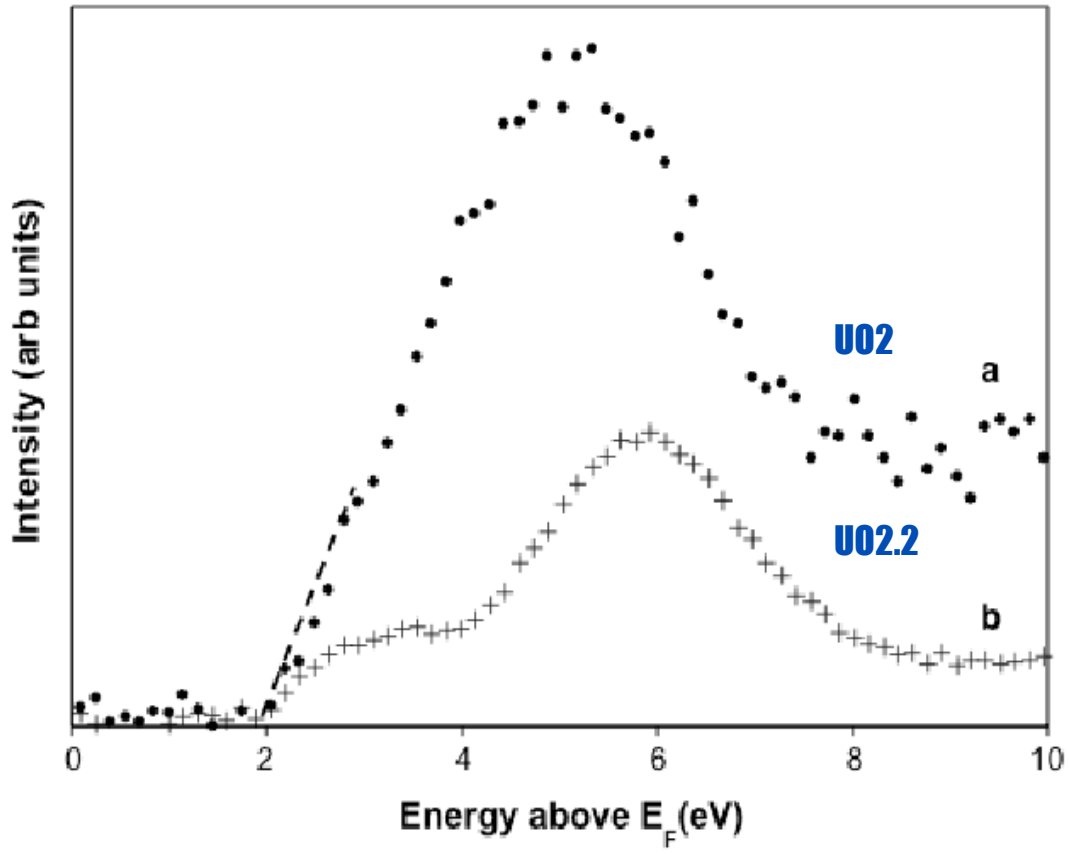


Fig. 3. Background subtracted IPS spectra of (a) UO_2 (dots) and (b) $UO_{2.2}$ (crosses). The dashed line on the UO_2 spectra represents the pre-peak attributed to the 6*d* states by Baer and Schones [6].

- Here, variation in the IPES with stoichiometry are being probed.
- The UO2 is in agreement with Baer & Schoenes and Chauvet and Baptist.
- Roussel, P. Morrall, and S. J. Tull, J. Nucl. Mater. 385, 53 (2009).

Grioni et al, RIPES of Uranium

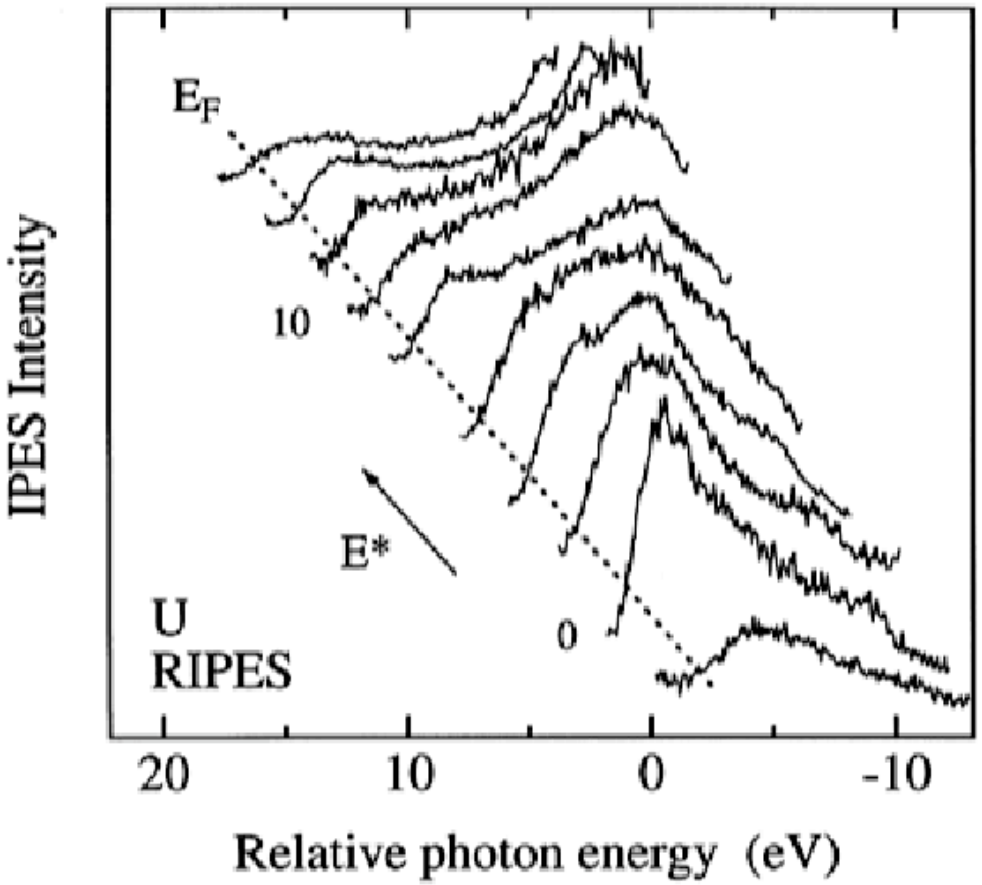


Fig. 7. RIPES spectra of metallic uranium, showing only a modest increase of intensity at the U N_5 (4d) edge.

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Resonant Inverse Photoemission: A New Probe of Correlated Systems

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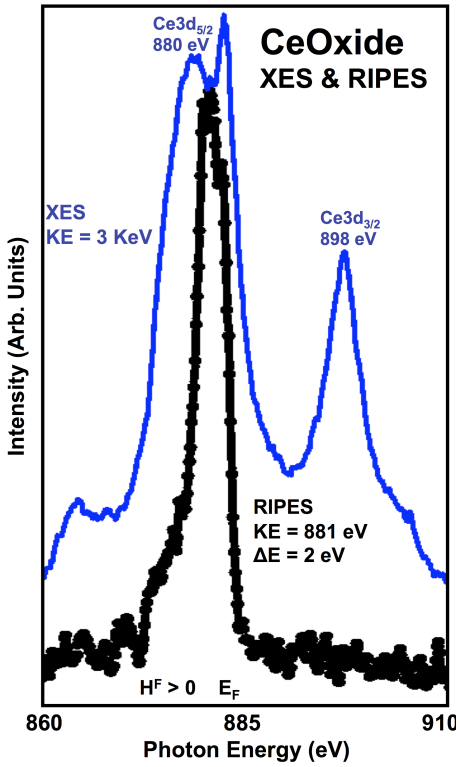
(Received 20 September 1993)

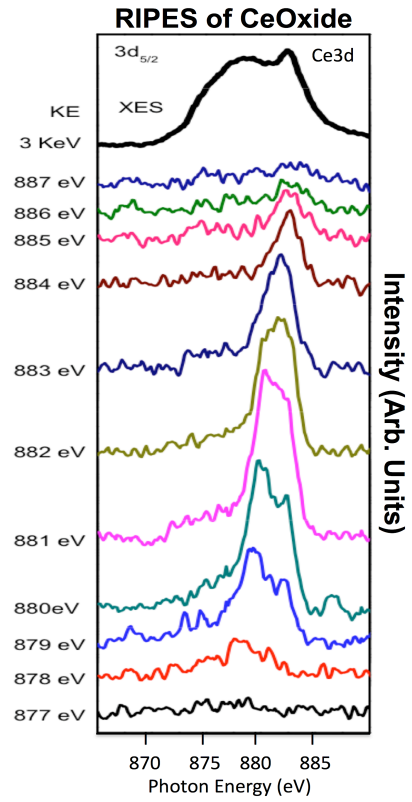
Inverse photoemission measurements of cerium compounds reveal a strong energy dependence near the Ce M_5 ($3d_{5/2} \rightarrow 4f$) absorption edge. Two separate resonances, resulting from configuration mixing in the ground state, are identified for the first time. Their relative intensities reflect the different hybridization strengths in various Ce-based materials. Because of its site and symmetry selectivity, resonant inverse photoemission is potentially a valuable technqiue for the investigation of correlated materials, complementary to the well-established resonant photoemission spectroscopy.

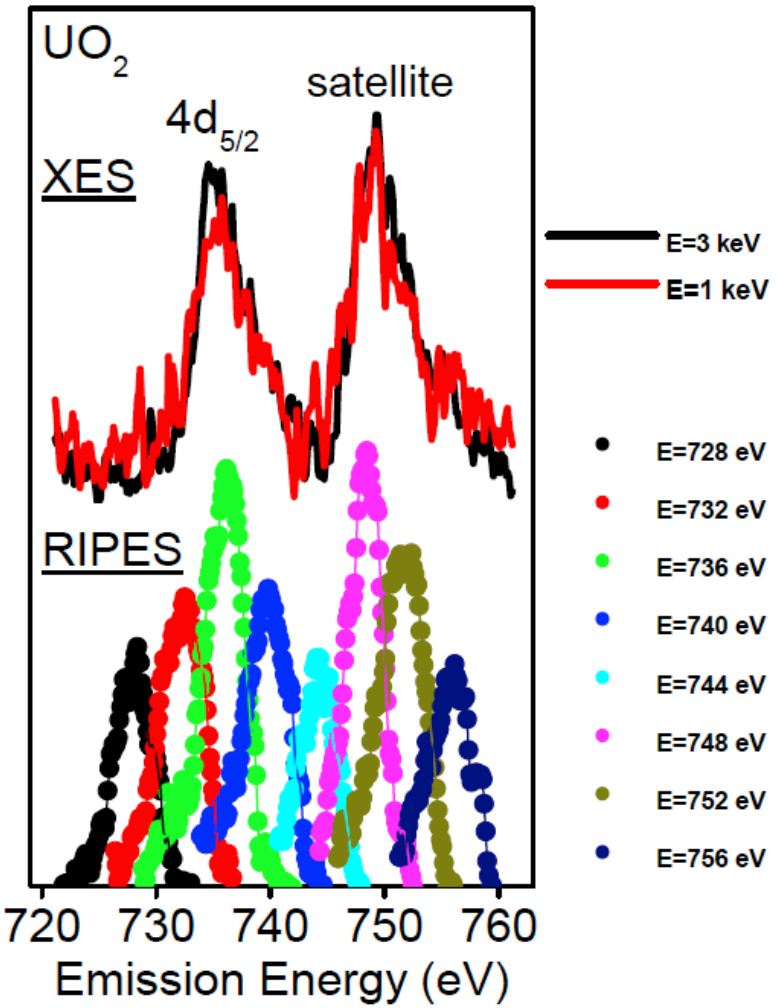
- **U RIPES is fairly weak…**
- **Grioni et al, J. El. Spect. & Rel. Phen. 101-103, 713 (1999)**
- **P. Weibel, M. Grioni, D. Malterre, B. Dardel, and Y. Baer, Phys. Rev. Lett. 72, 1252 (1994).**

RIPES of the Oxides of Uranium and Cerium

CeOxide-strong res; UO2-satellite…







J. G. Tobin, S.-W. Yu, B. W. Chung, G. D. Waddill, L. Duda and J. Nordgren, Phys. Re B 83, 085104 (2011)

Summary, Conclusions and Prospects

Most demanding & powerful actinide spectroscopy → soft x-ray and VUV photons

Relatively low energy and fairly small sampling depth:

→ un-encapsulated, highly cleaned and well prepared surface

→ myriad of sample containment problems for radioactive materials

Despite these hindrances and difficulties, the soft-x-ray and ultra-violet spectroscopy of the actinides can provide an amazing level of detailed information, particularly having to do with 5f electronic structure.

The subjects of discussion included: VUV photoelectron spectroscopy (PES), X-ray photoelectron spectroscopy (XPS),Synchrotron-radiation-based photoelectron spectroscopy, Soft x-ray absorption spectroscopy (XAS), Soft x-ray emission spectroscopy (XES), Inverse photoelectron spectroscopy (IPES), Bremstrahlung Isochromat Spectroscopy (BIS), Low energy IPES, Resonant inverse photoelectron spectroscopy (RIPES).

- **Our ultimate goal remains Pu and its electron correlation.**